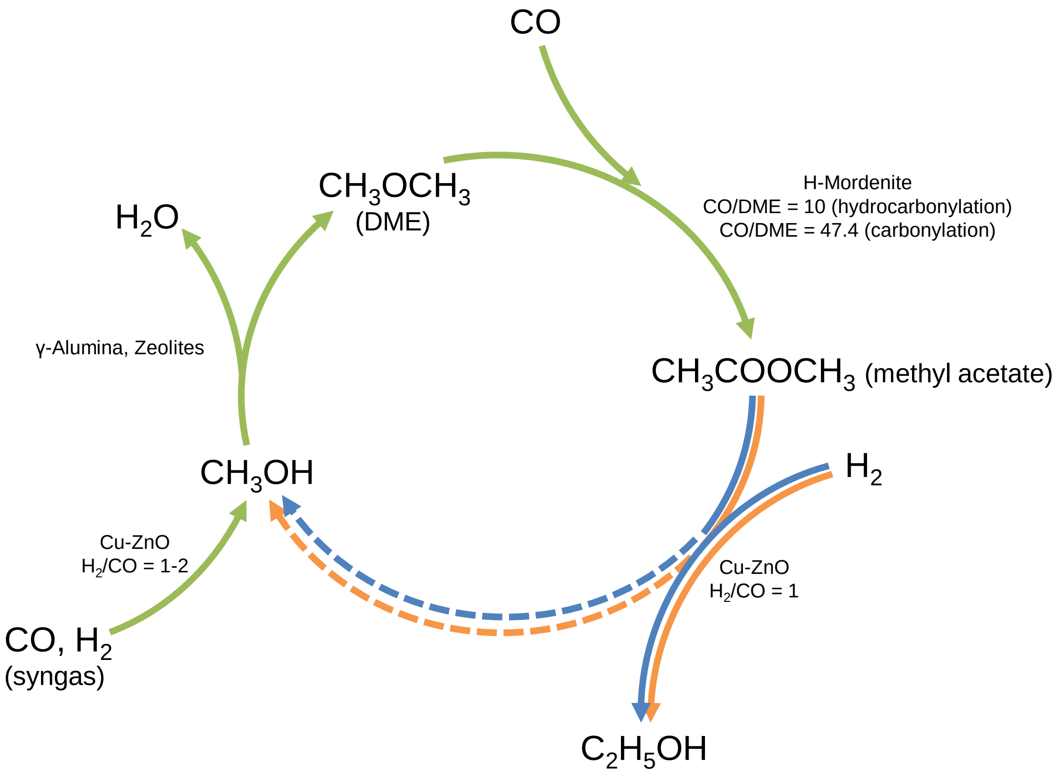
THERMOCHEMICAL BIOREFINERIES BASED ON DME AS PLATFORM CHEMICAL

Conceptual Design and Technoeconomic Assessment



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Thermochemical Biorefineries based on DME as platform chemical: conceptual design and technoeconomic assessment

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Biorrefinerías Termoquímicas basadas en DME como intermediario: diseño conceptual y análisis tecno-económico

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A mi madre

Contents

Abstract vii

Resumen viii

1. Introduction 1

1.1. Thermochemical Biorefineries 1

1.2. Current state of Thermochemical Biorefineries 6

1.3. Future development of Thermochemical Biorefineries through gasification 10

2. Objectives 11

3. History and context of the thesis 12

4. Methodology for the conceptual design and assessment of thermochemical biorefineries based on DME 14

4.1. Process design and technical assessment 14

4.2. Environmental sustainability assessment 14

4.3. Economic assessment 18

5. Results and discussion 22

5.1. Description of the concepts 22

5.2. Material, energy and economic results 27

5.3. CO_2 emissions, sustainability and BECCS 32

6. Conclusions and recommendations for further research 36

Paper 1: 39

Potential routes for thermochemical biorefineries

Paper 2: 77

Technoeconomic assessment of lignocellulosic ethanol production via DME hydrocarbonylation

Paper 3: 101

Technoeconomic assessment of potential processes for bio-Ethylene production

Paper 4: 133

Thermochemical Biorefineries with multiproduction using a platform chemical

Paper 5: 161

Thermochemical Biorefinery based on dimethyl ether as intermediate: Technoeconomic assessment

Paper 6: 191

Bio-syngas to gasoline and olefins via DME – A comprehensive technoeconomic assessment

Paper 7: 219

A proposal of methodology for the assessment of sustainability in thermochemical biorefineries: Application to thermochemical biorefineries based on dimethyl ether as a platform chemical

Annex A: 239

Supporting information of Paper 5

List of publications 253

Curriculum Vitae 254

Agradecimientos (Acknowledgements) 255

Abstract

This thesis deals with the conceptual design and assessment of thermochemical biorefineries (through gasification and mostly using DME as a platform chemical), combining the technical, economic, environmental and social (regulation) perspectives. Current projects of thermochemical biorefineries (BTL/G: biomass-to-liquid/gas process) are usually energy-driven and focused on the production of a single biofuel. In this thesis, a different concept is proposed: thermochemical biorefineries using a platform chemical, which is a new field of research focused on the co-production of fuels, chemicals, materials and services (heat and electricity) using lignocellulosic biomass. This kind of biorefinery benefits from potentially better energy and material integration, they are not limited to a single market (energy or chemical) and can produce high-value low-volume product (high-value chemicals) in large-scale facilities. **Paper 1** reviews the most important routes (for the design of thermochemical biorefineries) via a platform chemical including those known from petro and carbochemistry, and those recently developed. **Paper 2** assesses the use of DME as platform chemical for the synthesis of ethanol from lignocellulosic biomass. This indirect synthesis of ethanol from syngas using the DME hydrocarbonylation route overcomes the limitations of the production of ethanol via direct synthesis (low yield process), enhancing the global energy efficiency of biomass conversion and at milder operating conditions (pressure). **Paper 3** assesses the valorization of bioethanol for the production of ethylene as a precursor of plastics and commodities for the organic industry, which could not be produced so efficiently directly from syngas. Despite the conversion of ethanol (platform chemical) into ethylene being a mature technology, the use of bioethanol presents different uncertainties (origin of the bioethanol: 1st, 2nd generation, scale capacity and profitability) which are analyzed in this paper. **Paper 4** gives a general view of thermochemical biorefineries and a discussion of the main aspects of the design of thermochemical biorefineries with multiproduction using a platform chemical. The technical, economic, environmental and social (regulation) perspectives are discussed along with recommendations for the future development of thermochemical biorefineries. **Paper 5** assesses the design of a thermochemical biorefinery focused on multiproduction using DME as a platform chemical. The selected chemical routes are the carbonylation and hydrocarbonylation of DME. The co-production of a high-value low-volume product (e.g. methyl acetate) and a low-value high volume product (e.g. DME) achieves greatest profitability. **Paper 6** assesses the realization of a thermochemical biorefinery producing synthetic gasoline and ethylene through the combination (integration) of two direct routes from syngas producing synthetic gasoline and olefins from DME as a platform chemical. **Paper 7** gives a methodology for the assessment of sustainability based on European regulations, using the designs of **Paper 5**. The resulting savings of GHG emissions are greater than that required by European regulations and, therefore, two alternatives for the valorization of extra-avoided GHG emissions (extra saving) have been proposed: via the sale of CO_2 credits (extra-avoided emissions) and the co-feeding of fossil fuels.

Resumen

Esta tesis se centra en el estudio de biorrefinerías termoquímicas (instalación que procesa biomasa para la producción de una gran variedad de productos: combustibles para la producción de calor o electricidad, carburantes para la automoción, compuestos químicos, materiales, calor y/o electricidad) basadas en gasificación de biomasa. Hasta ahora el estudio de biorrefinerías termoquímicas se ha centrado en procesos de producción de combustibles líquidos (automoción) y gaseosos, generalmente orientados a un único producto (procesos BTL/G). Estudios clásicos de procesos BTL/G son la producción de diésel Fischer-Tropsch, bioetanol, metanol, hidrógeno y gas natural sintético (SNG). En estos procesos el gas de síntesis procedente de la gasificación es convertido directamente en el producto buscado. Esta síntesis directa presenta ciertos inconvenientes, en particular en la síntesis de bioetanol, donde la productividad es baja y la presión de operación elevada. Con el objetivo de mejorar la productividad del proceso, se ha planteado el uso de un intermediario de reacción (*platform chemical*). De esta forma el gas de síntesis sería primero convertido en el *platform chemical*, que posteriormente se convertiría (consumiendo más gas de síntesis) en el producto final (bioetanol). Se han revisado diversos *platform chemicals* para la síntesis indirecta de carburantes y químicos a partir de gas de síntesis y se han identificado las distintas rutas químicas con interés para una biorrefinería termoquímica. En el caso de la síntesis indirecta de etanol, la ruta de hidrocarbonilación de DME (dimetiléter) presenta la ventaja de que permite operar a presiones moderadas y con gran selectividad a etanol. En este proceso se genera también metanol como subproducto de la reacción. Sin embargo éste se puede convertir en más DME empleando los equipos ya existentes en la planta, por lo que su impacto es mínimo. Precisamente ésta característica (la fácil recirculación de los subproductos de la reacción) es la ventaja del uso de las rutas indirectas, que permite que las plantas compensen una mayor inversión respecto los BTL/G (más equipos para la conversión indirecta del gas de síntesis) con la mayor producción (la conversión global es superior a la de la síntesis directa). Particularmente, el DME ofrece una serie de ventajas como *platform chemical* respecto al resto de compuestos revisados. Usando la ruta de la hidrocarbonilación de DME se ha diseñado y evaluado la producción en una planta comercial (500 MW de biomasa) de bioetanol. Los resultados demuestran que se puede producir etanol a un precio inferior a los 0,45 €/L.

La multiproducción en una biorrefinería termoquímica permite la coproducción de una amplia gama de productos: combustibles para la producción de calor o electricidad, carburantes para la automoción, compuestos químicos (tanto *commodities* como de gran valor), materiales, calor y/o electricidad. El uso de un *platform chemical* también presenta importantes ventajas en este tipo de plantas y de hecho permite que la coproducción se pueda realizar sin merma de la eficiencia global del proceso. En la tesis se han diseñado y evaluado una serie de conceptos de biorrefinería termoquímica con multiproducción usando el mismo *platform chemical* (DME) que con la síntesis indirecta de etanol, por sus buenos resultados. En estos conceptos se han contemplado diversas combinaciones entre los siguientes productos: bioetanol (puede usarse

como substituto de la gasolina o como *commodity* para la producción de biobutanol o bioetileno), DME (substituto del diésel, del gas licuado del petróleo –calefacción–, o como *commodity* para la producción de olefinas), metilacetato (solvente y precursor del acetato de celulosa entre otros usos), hidrógeno (*commodity* o carburante) y electricidad. El posterior estudio tecno-económico de estos casos concluye que aquellos que coproducen metilacetato, un compuesto de gran valor en el sector petroquímico, ofrecen rentabilidades por encima del 20%. Este tipo de plantas se benefician de la economía de escala para la producción de un producto de gran valor pero en un volumen reducido. De esta forma la coproducción de un producto con un gran volumen y bajo precio junto con un producto de gran valor y bajo volumen (el precio del metilacetato es más del doble del resto de los productos contemplados) permite que la biorrefinería sea rentable y al mismo tiempo diversifica los sectores de negocio (reduciendo su dependencia de la evolución del mercado). La experiencia ganada en el diseño de biorrefinerías termoquímicas ha permitido la inclusión de un capítulo con recomendaciones para el estudio y diseño conceptual de plantas multiproducto.

Fruto de la colaboración con el *Karlsruhe Institute of Technology* (KIT, Alemania), se ha evaluado también un enfoque alternativo al desarrollado originalmente en esta tesis. El proyecto bioliq® contempla una alternativa distinta para la producción del gas de síntesis (pirólisis y gasificación EF con oxígeno a alta temperatura) y un escenario técnico-económico más conservador (escenario económico: precio biomasa). Se han diseñado y evaluado tres conceptos de biorrefinería termoquímica bajo las premisas del proyecto bioliq®, todos ellos usando DME como *platform chemical*: la producción de gasolina sintética, la producción de olefinas y la producción combinada de gasolina sintética y etileno. Estos conceptos, a pesar de que resultan desfavorables desde el punto de vista económico (debido al escenario del bioliq®), refuerzan lo ya evaluado en los anteriores conceptos de biorrefinería: compensación de los mayores costes de inversión debidos a la multiproducción por la integración energética y material.

La producción de etileno a partir de bioetanol se ha estudiado con el objeto de compararla con la producción de olefinas a partir de DME comentada antes. Diversos escenarios se han contemplado en función del origen de bioetanol. Así por ejemplo se ha analizado el uso de bioetanol comercial (1ª generación), de bioetanol de 2ª generación tanto el producido por procesado bioquímico (hidrólisis enzimática o fermentación de gas de síntesis) como por procesado termoquímico (síntesis directa o indirecta). Los resultados muestran que el mejor escenario es el que emplea bioetanol brasileño (escenario actual) o bioetanol por síntesis indirecta (escenario futuro).

La sostenibilidad de las biorrefinerías termoquímicas, al igual que la de la bioquímicas, no puede ser asumida per se. En el caso de esta tesis el estudio de la sostenibilidad se ha centrado en las plantas con multiproducción, ya que la diversificación de la producción (en especial por la producción de químicos) plantea dudas en la aplicación de la legislación Europea (Directiva 2009/28/EC). Se ha propuesto una metodología que incluye la ponderación de los distintos productos y servicios, así como el tratamiento de las emisiones en el uso final de los mismos. Los resultados de la aplicación de la metodología propuesta y de la metodología sin adaptar de la UE demuestran que los conceptos analizados cumplen con los requisitos de sostenibilidad. Además, en todos los casos, la emisiones de gases de efecto invernadero son inferiores (o muy inferiores) al límite establecido por lo que se ha estudiado la posible venta de derechos de emisión asociados a esta reducción extra. La incorporación de BECSS (captura y secuestro de CO_2 en biorrefinerías) también ha sido analizada en la mayoría de los conceptos de biorrefinería termoquímicas, que se ven favorecidos de un bajo coste de captura de CO_2 respecto a las plantas convencionales de potencia. La captura de CO_2 en biorrefinerías termoquímicas permite que se lleguen a alcanzar emisiones negativas.

El trabajo futuro en el ámbito de las biorrefinerías termoquímicas se debería enfocar al diseño y evaluación de nuevos conceptos de biorrefinería usando otras rutas y distintos *platform chemicals*. El uso de biomasa puede contribuir significativamente a la reducción de emisiones de gases de efecto invernadero y la producción de químicos sería clave en una reducción acelerada de dichas emisiones. Sin embargo, la reducción de emisiones en la producción de bio-químicos todavía no ha sido regulada.

1. Introduction

The development of new industrial processes is a core subject of research centers. A doctoral thesis in process design should aim to contribute to the development of new processes taking into account the combination of the technical, economic and environmental perspectives. The conversion of biomass into usable products, which could substitute or replace those from fossil fuels, is one of the trending topics in the energy sector. The generated knowledge could be used by the industry for the realization of new commercial plants via public projects, joint ventures or mixed private-public funding projects. The experience of biochemical biorefineries (bioethanol) is an example of how the industry could benefit from academic research; and that could apply to thermochemical biorefineries.

The advantages and disadvantages of using biomass as a renewable energy source have been widely discussed and this thesis does not aim to contribute to the elaboration of such discussion. Hence, fundamental aspects about biomass, i.e. uses, diversity, availability, composition, etc., are not considered (no more can be added to the references in the literature). Therefore, the discussion is from the beginning focused on the novelty of thermochemical biorefineries and their potential to produce *cost-competitive* products, equivalent to those currently used (from fossil feedstock), but *sustainably*.

1.1. Thermochemical Biorefineries

A thermochemical biorefinery is a facility, which processes biomass by means of pyrolysis and/or gasification to produce fuels (transportation, for heat/electricity generation), chemicals, materials and services (heat, electricity). In a thermochemical biorefinery, the production can be focused either on a single product, e.g. FT-diesel, or on a mix of products (multiproduction). The first alternative usually refers to the term BTL/G (biomass-to-liquid/gas) process, whereas the second (a thermochemical biorefinery with multiproduction) is of recent interest. There are several pilot and demonstration plants based on BTL/G processes. However, research on thermochemical biorefineries with multiproduction is limited and there are not active projects for the realization of pilot plants. This thesis focuses on the case of thermochemical biorefineries through gasification and therefore the case of plants through pyrolysis is only briefly mentioned.

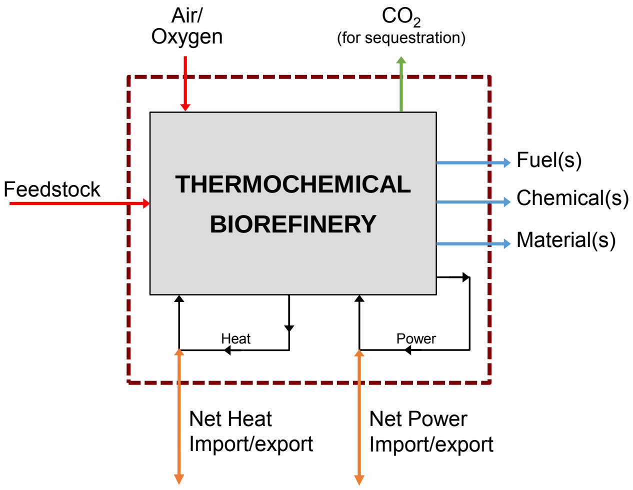


Figure 1. Short scheme of a thermochemical biorefinery through gasification.

In a thermochemical biorefinery, the biomass feedstock is pretreated by drying and sizing (grinding, milling) and sometimes torrefacted. Regarding the case, it can be pyrolysed (fast pyrolysis) or gasified, although if a pressurized gasifier is selected, sometimes it is preferable to pyrolyse the biomass in the pre-treatment. In the case of being pyrolysed, it would result in a liquid (bio-oil), a gas (volatiles) and a solid (char). The bio-oil could be further processed in order to obtain transportation fuels, and this processing could be completely or partially carried out in conventional refineries (hydrotreating). The volatiles are usually combusted in the pyrolysis plant in order to satisfy the internal demand for heat and electricity. In the case of biomass gasification, the resulting gas, synthesis gas (syngas), is converted into products via catalytic synthesis or used for power generation.

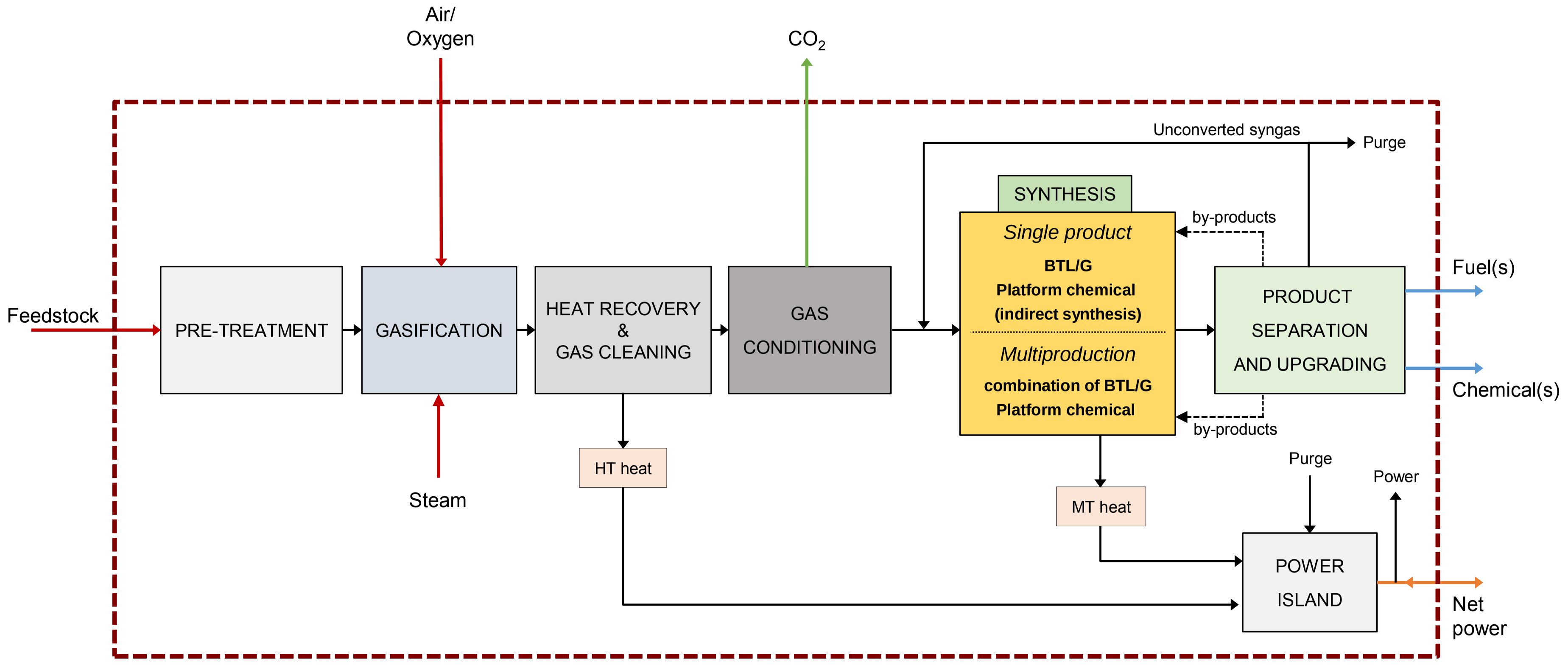
Nowadays, the maximum capacity of (pre-)commercial gasifiers is too low to construct profitable thermochemical biorefineries. Among the gasification technologies, there are three appealing options for thermochemical biorefineries:

- The i-CFB (dual bed, indirectly-heated circulating fluidized bed) gasifier, which operates at temperatures of 800–850ºC and atmospheric pressure. It generates tars and light hydrocarbons. The pretreatment of biomass is reduced.
- The CFB gasifier using oxygen and steam at medium pressure (17 bar) and temperature (800ºC). It generates tar and light hydrocarbons. The pretreatment of biomass is more problematic.
- The EF (entrained–flow) gasifier, which operates at the highest temperature (1200ºC) and high pressure (40 bar). It generates neither tars, nor light hydrocarbons, although it requires the most problematic biomass pretreatment, as in the bioliq® concept [*see Paper 6*].

In a broader sense, the CFB technology is an intermediate technology between the i-CFB and EF; and it has not been included in this thesis. It is assumed that the results of the CFB technology lie between i-CFB and EF.

The raw syngas from the gasifier may contain some organic materials, tars, and inorganic compounds: HCl, NH_3, H_2S that must be removed (or converted) before conditioning for synthesis. In some gasifiers (EF) there are not tars, however, in the case they are in the raw syngas (CFB), two options are available. First, oil scrubbing would reduce the tar content up to the limit for further processing. There are some commercial technologies available. Second, a tar reformer would be able to convert all the tar into more syngas along with the light hydrocarbons (mainly methane) in the raw syngas. However, tar reformers are still not commercial. The conditioning of the cleaned syngas depends on the selected synthesis route (chemical route). Frequently, the H_2/CO molar ratio of the cleaned syngas does not fit the optimum value for the synthesis and a WGS could be used to modify (increase) the ratio. Nonetheless, in the case of a high concentration of hydrocarbons in the syngas, e.g. case of using oil-scrubbing, the use of a *reformer* unit will combine the correction of the H_2/CO ratio and the conversion of the hydrocarbons. There are different technologies for the *reformer* unit: POx (partial oxidation), ATR (auto-thermal reformer) and SMR (steam reformer); and the selection should be carefully studied. In the conditioning of syngas, it is possible to capture CO_2 (pre-combustion) at a lower cost than in conventional power plants (post-combustion). Furthermore, if a POx or a ATR unit is used, the capture is usually mandatory in order to avoid excessive accumulation of CO_2 in the synthesis loop.

The synthesis section is designed for the production of a single product or for multiproduction, commonly including the recycle of unconverted syngas (see Figure 2). The single production is accomplished through the use of a syngas-to-product route (direct route, BTL/G process), or via a platform chemical (intermediate) using a syngas-to-platform-to-product route (indirect route). Multiproduction is achieved through the combination of several direct routes (the syngas is split into different reaction steps), which would be the combination of different BTL/G processes; or using a platform chemical, through the combination of different chemical routes sharing the platform chemical (the syngas is converted into a platform chemical, which is further diverted into several reaction steps). In the case of multiproduction without a platform chemical, the potential integration is poor (usually limited to energy). However, in the case of using a platform chemical there is great potential for material and energy integration. The generation of services (heat and electricity) is mainly carried out in the power island, although heat integration within process streams is also possible. Frequently, there is an excess of low-quality heat in the plant from the synthesis section (syngas conversion is usually exothermic and the reaction temperatures below 250ºC).


Air/
Oxygen
CO_2
Feedstock
PRE-TREATMENT
GASIFICATION
Steam
HEAT RECOVERY
&
GAS CLEANING
HT heat
GAS
CONDITIONING
Unconverted syngas
Purge
SYNTHESIS
Single product
BTL/G
Platform chemical
(indirect synthesis)
Multiproduction
combination of BTL/G
Platform chemical
by-products
by-products
MT heat
PRODUCT
SEPARATION
AND UPGRADING
Fuel(s)
Chemical(s)
Purge
Power
POWER
ISLAND
Net
power

1.1.1. Comparison of thermochemical and biochemical biorefineries

A biochemical biorefinery is a facility, which converts biomass by means of mechanical, chemical and/or biological processes. In a biochemical biorefinery, the processing and the potential products are intimately related to the biomass feedstock. This kind of biorefinery is similar to what can be found in the food processing industry and others like the paper or natural fiber industries. In biochemical biorefineries, the different components of the biomass feedstock are extracted and further purified and/or converted. Biochemical biorefineries are currently mostly limited to ethanol plants (using both 1^{st} and 2^{nd} generation processes) and the new proposals consider the co-production of chemicals (high-value compounds) and materials. The challenge in biochemical biorefineries is the optimization of processing (e.g. use and recovery of enzymes, efficient hydrolysis, reduction of pretreatment) and the incorporation of new microorganisms/enzymes for the biological/biochemical conversion of the different biomass fractions (especially lignin).

Processing in thermochemical biorefineries is similar to that carried out in conventional petrochemical facilities. For instance, the routes for syngas conversion come from previous research on carbochemistry and natural gas-to-liquids processes. In thermochemical biorefineries, there are no differences between different biomass crops and the diversity of the biomass feedstock is reduced to a single platform (bio-oil or syngas). Hence, thermochemical biorefineries will not be able to compete with biochemical biorefineries for the production of e.g. cosmetic products and some materials (natural fibers) and food additives (omega-3). However, thermochemical biorefineries could produce the same products or equivalent to those currently used for the energy (transportation, heat) and chemical (plastics, solvents, fibers, etc.) sectors. Current thermochemical biorefineries focus mainly on the single production of a transportation fuel, i.e. they are energy-driven biorefineries. The challenge in thermochemical biorefineries is the production, cleaning and conditioning of syngas in order to allow further conversion using the same processing as in a petrochemical facility. Furthermore, a challenge is the optimization of the chemical routes and the search for new routes for the conversion of syngas into valuable products achieving high-energy efficiency and profitability.

The biochemical biorefineries producing ethanol are commercial due to the availability of commercial equipment and the mild conditions of pressure and temperature for the processing of biomass. In biochemical biorefineries, the required (lower) investment allows the achievement of profitability on a smaller-scale. However, in thermochemical biorefineries the operating conditions are severe, involving a high investment cost. Hence, thermochemical biorefineries require of a larger scale in order to be profitable. The required equipment for the thermal processing (pyrolysis and gasification) is still not fully commercial. Furthermore, there are uncertainties surrounding the cleaning and conditioning of both bio-oil and syngas that could increase the investment cost, making the process unprofitable. These characteristics of thermochemical biorefineries are slowing their development.

1.2. Current state of thermochemical biorefineries

The analysis of the current state of thermochemical biorefineries is divided into the concepts of thermochemical biorefineries that have been proposed by research centers and the demonstration and commercial projects that are active worldwide. The realization of thermochemical biorefineries is still focused on the validation of primary thermochemical process technologies and the cleaning/conditioning of syngas and bio-oil.

1.2.1. Proposed concepts of thermochemical biorefineries

Table 1 shows a selection of the different concepts of a thermochemical biorefinery, which can be found in the literature. The concept that has received most attention is the BTL/G (plants focused on single production without using a platform chemical; i.e. direct routes), producing biofuels (ethanol, FT-diesel, DME, SNG, hydrogen). Concepts considering multiproduction are not so frequent and limited to the combination of direct routes from syngas. In recent years, the combination of biochemical and thermochemical processing has become increasingly of interest as integrated plants (*two-platform* biorefinery) or via the fermentation of syngas produced by gasification (combination of the biochemical and thermochemical processing).

1.2.2. Demonstration and commercial projects of Thermochemical Biorefineries (process realization)

North America and Europe are the focus of the current realization of thermochemical biorefineries, where the projects based on gasification dominate over those using pyrolysis. All active projects focus on the single production of a transportation fuel (biofuel) mostly using the BTL/G concept. Nonetheless, there are two exceptions of relevance. In Europe, the bioliq® project focuses on the production of synthetic gasoline via DME (platform chemical) based on a commercial (petrochemical) technology: MTG [*for further details see Papers 1 and 3*]. This project is public funded by the German Government and the European Union (www.bioliq.de, www.bioboost.eu). In North America, Enerkem Inc. has developed an indirect route for the production of ethanol via methanol (as a platform chemical). Enerkem has pilot and demonstration plants in Canada and commercial plants are under construction or recently inaugurated in Canada and USA (www.enerkem.com). However, there is no confirmation of the production of ethanol in those plants.

Table 1. Main research groups that have designed and assessed thermochemical biorefineries (public access).

Concept	Processing	Research center	Product(s)
Single production, BTL/G	Thermochemical (pyrolysis and gasification or only gasification)	Chalmers University of Technology, Sweden	Methanol
		Industrial Energy Systems Laboratory, EPFL, Switzerland	SNG Methanol DME FT-diesel Hydrogen
		NREL, USA	Ethanol FT-diesel Synthetic gasoline
		PNNL, USA	Ethanol Synthetic gasoline
		Princeton University, USA	Methanol Hydrogen
		The Technical University of Denmark (DTU)	DME
		University of Seville (BEGUS group), Spain	Ethanol
		Utrecht University, The Netherlands	Methanol FT-diesel Hydrogen
		VTT, Finland	Gasoline Olefins FT-diesel
	Thermochemical (pyrolysis)	Thermo-Chemical Conversion of Biomass Group, University of Twente, The Netherlands	Diesel
Single production via a platform chemical	Thermochemical (pyrolysis and gasification) Platform chemical: DME	Karlsruhe Institute of Technology (KIT), Germany	FT-diesel Synthetic gasoline
		University of Seville (BEGUS group), Spain	Ethanol Ethylene
	Thermochemical (gasification) Platform chemical: Acetic acid	PNNL, USA	Ethanol
	Thermochemical (pyrolysis and gasification) Platform chemical: Ethanol	University of Seville (BEGUS group), Spain	Butanol Ethylene

Table 1. Main research groups that have designed and assessed thermochemical biorefineries (public access) [*continued*].

Multiproduction, combination of BTL/G processes	Thermochemical (gasification)	ECN, The Netherlands	SNG, ethanol
		The Princeton University, USA	FT-diesel, synthetic gasoline, kerosene
		The University of Nottingham, Malaysia	DME, FT-fuel, methanol, higher alcohols
		Utrecht University, The Netherlands	FT-liquids, methanol, urea
Multiproduction via a platform chemical	Thermochemical (pyrolysis and gasification) Platform chemical: DME	Karlsruhe Institute of Technology (KIT), Germany & University of Seville (BEGUS group), Spain	Ethylene, synthetic gasoline
	Thermochemical (gasification) Platform chemical: DME	University of Seville (BEGUS group), Spain	Ethanol, DME, methyl acetate, hydrogen
Combination of biochemical and thermochemical processing	Biochemical (fermentation) and thermochemical (gasification): *two-platform* biorefinery	Chalmers University of Technology, Sweden	Ethanol, DME, paper
		Princeton University, USA	Ethanol, FT diesel and power Ethanol, FT diesel and SNG Ethanol and hydrogen Ethanol, proteins and power Ethanol, proteins and FT diesel
	Thermochemical (gasification) and fermentation of syngas	DIPIC, University of Padova, Italy	Ethanol

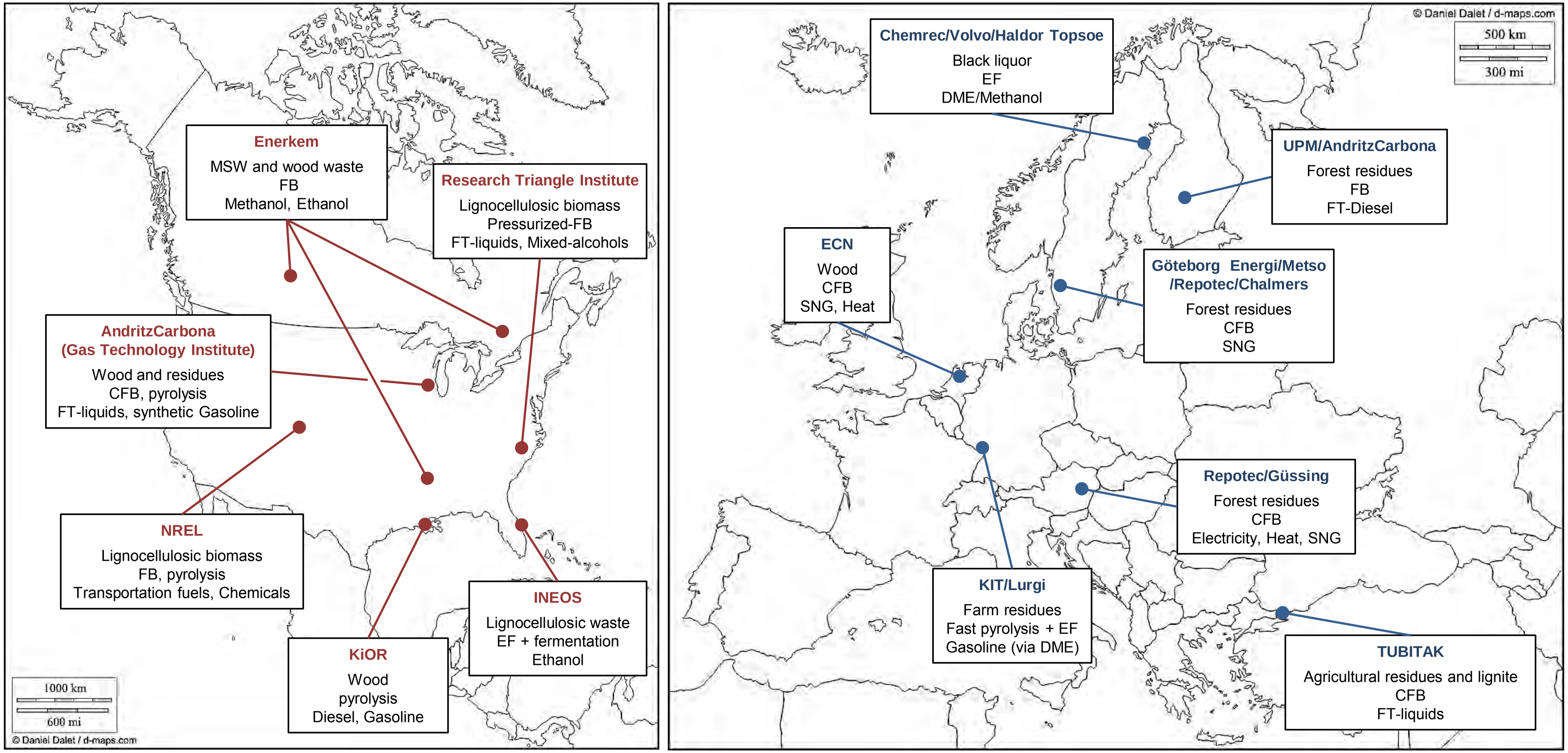


Figure 3. Main active projects of thermochemical biorefineries. Elaborated from [1-3].

MSW: municipal solid waste

CFB: circulating fluidized bed; EF: entrained-flow; FB: fluidized bed [gasifiers]

FT: Fischer-Tropsch; DME: dimethyl ether; SNG: synthetic natural gas

1.3. Future development of Thermochemical Biorefineries through gasification

The future development of thermochemical biorefineries through gasification depends on the commercialization of technologies for biomass conversion on a large scale (> 500 MW_{th}). These technologies, however, still require intensive and costly development. Assuming that the technologies are available, the estimated investment for a first commercial plant of 500 MW_{th} of biomass input would be 250–350 M€ [*see Papers 2, 3, 5 and 6*]. This huge investment, along with the market uncertainties concerning the demand and the prices of their products, results in a great financial risk. Therefore, the public sector should contribute to the development of the technologies for biomass conversion and to the realization of the first commercial plants.

Another factor is the regulation of the bio-energy sector (including all kind of biomass-derived products and services). There are great uncertainties surrounding the economic scenario for bio-products. In the case of thermochemical biorefineries (compared to biochemicals), it is even worse, since their capacity is larger. Hence, the regulation of the bio-energy sector must secure large investment for the construction of the first plants. It can be done via quotas, tax reductions or direct subsidies. Regulation should be reliable, permanent and, if possible, international, so the investors feel confident.

Regarding other uncertainties in the future development of thermochemical biorefineries, the supply of large amounts of biomass (a plant of 500 MW_{th} requires more than 2000 tonnes of dry biomass per day) and the optimization of syngas conversion into products are of great interest. Thermochemical biorefineries focused on multiproduction can achieve important benefits and therefore contribute to the future development of thermochemical biorefineries. The co-production of transportation biofuels, biofuels for heat generation (domestic use), chemicals (commodities and high-value compounds), materials, heat and electricity brings lower production costs, since the process is energy and material integrated enhancing the efficient conversion of syngas. Furthermore, it reduces the dependence of the biorefinery to a single market (e.g. in the case of single production of bioethanol). In a thermochemical biorefinery, the same or equivalent chemicals as those produced in the petrochemical industry are produced; contrary to biochemical biorefineries which are able to produce high value products with a small market or products that might substitute those of fossil origin but whose production is not competitive. Hence, thermochemical biorefineries producing chemicals could actually sell chemicals in the regular market.

2. Objectives

This thesis aims to propose new concepts of a thermochemical biorefinery and to assess if they are feasible, profitable and sustainable (technoeconomic and environmental sustainability assessment). In order to conduct this objective, the specific targets of the thesis are:

- The identification of available chemical routes for the design of new concepts of thermochemical biorefineries using a platform chemical (Paper 1).
- The technoeconomic assessment of the indirect synthesis of ethanol using DME as a platform chemical (Paper 2).
- The technoeconomic assessment of the production of ethylene from biomass, using ethanol and/or DME as a platform chemical: ethanol dehydration or DME-to-olefins (Paper 3).
- The conceptual design of thermochemical biorefineries with multiproduction using a platform chemical (Paper 4).
- The design, technoeconomic and sustainability assessment of different concepts of thermochemical biorefineries using DME as a platform chemical for the co-production of transportation fuels, electricity and chemicals (Paper 5).
- The design and technoeconomic assessment of the production of gasoline, olefins and the combined production of gasoline and ethylene using DME as a platform chemical (Paper 6).
- The proposal of a methodology (based on the European methodology) for the assessment of sustainability in thermochemical biorefineries with multiproduction (Paper 7).
- The assessment of sustainability of the concepts of thermochemical biorefinery using DME as a platform chemical for the co-production of transportation fuels, electricity and chemicals (Paper 7).

3. History and context of the thesis

At the beginning of the doctoral training in 2009, the research activities of BEGUS in the field of thermochemical processing of biomass were limited to the improvement of the synthesis of ethanol using biomass-derived syngas (direct route). The group was involved in I+DEA project (funded by Abengoa Bioenergy and the Ministry of Science and Innovation), with the aim of creating the conceptual design of a thermochemical biorefinery producing bioethanol (a BTL/G process). Previously, within RENEW project (6th Framework Programme), catalysts for the direct synthesis of ethanol from syngas had been developed. The further development and optimization of such catalysts (extensively tested) resulted in a patent of Abengoa Bioenergy. Despite the advantages of the developed catalyst, the productivity of ethanol was still limited by the generation of by-products. Because of this, other chemical routes were identified for the synthesis of ethanol from syngas, but indirectly. These routes use an intermediate, which is synthetized from syngas and further converted into ethanol. The first proposed intermediate (platform chemical) was methanol and the (indirect) route was the homologation of methanol. However, within BIOSOS project (funded by Abengoa Bioenergy and the Ministry of Science and Innovation), DME was identified as a better candidate. The research group of Prof. Tsubaki proposed in 2010 a new indirect route using DME, the hydrocarbonylation route. This route seemed appealing, since it avoided the use of homogenous catalyst and the operating pressure was reduced. Taking the experimental data of the DME hydrocarbonylation, a design of a thermochemical biorefinery was proposed and the results of the technoeconomic assessment showed that the indirect synthesis of ethanol via DME achieves better profitability than the direct route (previously assessed in I+DEA project).

A common characteristic of the indirect routes for ethanol synthesis is that they are able to overcome the low yield to ethanol of direct synthesis. The idea of the indirect synthesis of ethanol was not new, although the use of DME had not been previously assessed. In the preliminary optimization of the plant (indirect synthesis of ethanol) the “electric energy neutral” criterion, i.e. it allows neither the import nor the export of electricity, was imposed as in I+DEA and BIOSOS projects. However, this criterion was found to work against the maximization of the profitability of the biorefinery. A set of case studies was designed in order to evaluate the impact of process optimization (e.g. maximum conversion of syngas) in the profitability of the plant regardless of the electric balance. The results were satisfactory and they served as grounds for the re-thinking of the rules of thumb in the design and assessment of BTL/G processes. *What would happen if not all the platform chemical is converted in the plant?* It could be sold as a co-product. In the DME hydrocarbonylation route, the imposition of the complete conversion of the DME into ethanol penalizes the energy efficiency of the plant (it forces extensive recycling in the synthesis section). Nonetheless, as DME was also co-produced, the syngas could be efficiently converted and the investment cost reduced. This result inspired the design of 12 concepts of thermochemical biorefinery co-producing ethanol, methyl acetate, DME, hydrogen and electricity.

Despite thermochemical biorefineries with multiproduction using a platform chemical seemed to be a profitable alternative to BTL/G plants, sustainability had not been assessed. In common BTL/G studies, sustainability of the plant is assumed, since electricity is not imported and they have a single product. However, in the proposed concepts of a biorefinery there is not a limitation for the import of electricity and there is a mix of products, so the assessment of sustainability was mandatory. However, such assessment (in the form of a life cycle assessment of GHG emissions) has resulted in more than what was firstly envisaged. The current methodology (EU) refers only to biofuels and mainly to single product plants. Therefore, an update of the methodology was necessary in order to assess sustainability in the proposed concept of multiproduction plants. In this methodology, the treatment of bio-chemicals is a core subject, since they are not combusted in their final use.

During 2012, I visited the Karlsruhe Institute of Technology (KIT) in Germany under the supervision of Dr. Stahl (Institute of Catalysis Research and Technology –IKFT–). The research stay allowed the assessment of multiproduction plants in the framework of the bioliq® concept, e.g. a plant co-producing synthetic gasoline and ethylene via DME. Furthermore, this collaboration was further extended for the analysis of the production of ethylene using DME and/or ethanol as a platform chemical.

At the end of this thesis in 2013, a new public project, BIOTER (*BIOrrefinería TERmoquímica basada en DME*) has been granted to BEGUS for the further assessment of new concepts of thermochemical biorefineries using DME as a platform chemical.

4. Methodology for the conceptual design and assessment of thermochemical biorefineries based on DME

4.1. Process design and technical assessment

All process concepts have been designed using data from both research literature (mainly of BTL/G processes) and technology owners. Furthermore, all of them use a platform chemical for the production of a single product (Papers 2 and 3) or for multiproduction (Papers 5 and 6). The general rules of design are taken from important references of process engineering [4, 5]. However, for the design of processing areas like that of syngas conversion (synthesis) and the separation of products further rules of design are given in the thesis (Paper 4). The calculations for the material and energy balance have been carried out using the process simulation software Aspen Plus (Aspen Technologies Inc.). The modeling of the processing units is made by the selection of the appropriate thermodynamic method as discussed in each paper.

4.2. Environmental sustainability assessment

4.2.1. Status and regulation of sustainability in the European Union

The European Union has fixed a set of objectives in the framework of climate change and renewable energies[*]. The status of thermochemical biorefineries and the proximity of the target (2020) make it unlikely that thermochemical biorefineries could have an important role in the consecution of these objectives in Europe. However, in the development of current and future concepts of thermochemical biorefineries, the expected regulations on biomass utilization, bioenergy, bioproducts (biofuels and bio-chemicals), biorefineries, sustainability and GHG emissions are a core subject.

In Europe, the main regulation for the bioenergy sector is Directive 2009/28/EC [6], which gives the criteria for the assessment of environmental sustainability in biorefineries. However, the Directive does not include the possibility of the co-production of transportation fuels and bio-chemicals. Furthermore, the Directive does not consider the potential negative emissions if for example a plastic is produced using a chemical produced in a biorefinery. Future regulation should include these points along with others such as the indirect land-use change and the emissions in the final use of bio-products (currently neglected).

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[*] The Europe 2020 targets (climate change and renewable energies) are:

- 20% Greenhouse gas reduction.
- 20% Energy efficiency increase.
- 20% Renewable Energy with 10% renewable transportation fuels in transportation sector.
- 35% Greenhouse gas reduction of transportation biofuels compared to fossil fuels, increasing via 50% (2016) to 60% (2018).

4.2.2. Proposed methodology for thermochemical biorefineries with multiproduction

The assessment methodology is based on the European regulation on sustainability for biofuels and bioliquids (Directive 2009/28/EC, [6]) and it incorporates bio-chemicals assuming the same target saving of GHG emissions[†] [*further details of the methodology can be found in Paper 7*].

The Directive gives a general formula for the calculation of GHG emissions of biofuels and bioliquids:

$$E = e_{ec} + e_{l} + e_{p} + e_{td} + e_{u} - e_{sca} - e_{ccs} - e_{ccr} - e_{ee} \text{ (g } CO_2 \text{ equivalent / MJ of biofuel)}$$

This formula does not consider bio-chemicals as potential products. In order to do so and to include the possibility of multiproduction, a different (but equivalent) version is used:

$$E_m = E' + \text{sum}[x_i \cdot (e_{td,i} + e_{u,i})] \text{ (g } CO_2 \text{ equivalent / MJ of all co-products and services)}$$

$$E' = e_{ec} + e_{l} + e_{p} - e_{sca} - e_{ccs} - e_{ccr}$$

$$E_i = x_i \cdot E' + e_{td,i} + e_{u,i} \text{ (g } CO_2 \text{ equivalent / MJ of i)}$$

The saving of GHG emissions should also be modified for the inclusion of multiproduction, since there is a different fossil reference for each co-product and service (electricity). Then, an individual saving could be calculated for each co-product, the global saving being the weighted average:

$$\text{Saving}_i = (E_{Fi} - E_i)/E_{Fi}$$

$$\text{Saving} = \text{sum}(x_i \cdot \text{Saving}_l)$$

If there is an extra saving (regarding the minimum 60% commitment by the EU for 2018 [6]), it is calculated using the following expression:

$$\text{Extra saving} = \text{sum}(x_i \cdot E_{Fi}) \cdot 60\% - E_m \text{ (g } CO_2 \text{ eq/MJ of all co-products and services)}$$

The extra saving can be translated into an economic benefit in different ways. In this study only two options are analyzed: (1) via CO_2 credits (emission trading), and (2) via the co-feeding of a fossil fuel. The equivalent amount of CO_2 that is saved above the limit regulated is an extra-avoided emission[‡], which could be sold in emission trading. The co-feeding of coal (or other fossil fuels) will reduce the saving by introducing non-biogenic carbon into the biorefinery; the

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[†] Different targets are possible and, for example, BRIDGE [now "The Bio-based Industries Consortium"], a public private partnership (PPP) in the EU, proposes a saving of 50% for bio-based chemicals (http://bridge2020.eu/).

[‡] It is assumed that a reduction of GHG emissions larger than that required could be used for the enhancement of profitability via the sale of CO_2 credits (emissions trading). The avoided emissions include the potential negative emissions (net outlet of equivalent CO_2 from the atmosphere).

amount to reach the limit of the regulation is the maximum amount of coal that can be co-fed in order to achieve sustainability.

$$\text{Extra-avoided emissions (g } CO_2 \text{ eq/s)} = \text{Extra saving} \cdot \text{Total production (MW)}$$
$$\text{Co-feeding of coal } (MW_{th}) = \text{Extra saving} / (E_{F,coal} + \text{Extra saving} / \text{Plant capacity})$$

The value of e_u (emissions from fuel use) is defined as zero in the Directive [6]. The EU regulation, as well as equivalent regulations, assumes that the emissions of biofuels due to their final use have a neutral impact on GHG emissions. It is assumed that the GHG emissions in the combustion of biofuels are equivalent to the CO_2 assimilated by the growth of the biomass used for their production. However, in the combustion of biofuels, as well as in the combustion of petrol gasoline and diesel, there is an important fraction of other gases than CO_2 with GWP (global warming potential) like NOx, CO and VOC. These emissions, despite coming from a renewable carbon source, should not be neglected, since they have a larger GWP than CO_2. In this study, an approximation of the real value of the GWP of the co-products is given regarding the final use of each co-product.

In the calculation of e_u, the emissions of GWP gases different to CO_2 are considered as having a net emission to the atmosphere. These emissions are different in the case of the use of the same fuel as a transportation fuel or as a fuel for heat generation. In the case of bio-chemicals, there is not combustion of the product but a transformation into a different product (or directly used). In this case, the final use of the bio-chemical must be specified along with its GWP. As there is no combustion of the bio-chemical, the carbon content (in g of CO_2 referring to its complete combustion) should be added as a negative contribution in e_u. The average negative contribution producing a bio-chemical also requires the estimation of the emissions of the final disposition of the bio-chemicals (e.g. recycling, landfill). In this study, the emissions due to the final disposition of bio-chemicals (or the final products manufactured using them, e.g. plastics) are assumed to be 50% (average) of their equivalent CO_2 content. For electricity, the e_u is assumed zero, since the use of electricity gives no direct emissions.

4.2.3. Incorporation of BECCS

The incorporation of BECCS (Bioenergy with Carbon Capture and Storage) is assessed in Papers 3, 4, 6 and 7, using data from the IEA (International Energy Agency) for the transportation and storage of CO_2. The IEA has stated that the incorporation of BECCS could not only contribute to a reduction of GHG emissions but that it is mandatory if a net outlet of GHG from the atmosphere (negative emissions) is sought under the Kyoto Protocol [7]. The incorporation of BECCS in thermochemical biorefineries needs a translation into an economic benefit for biorefineries in order to make reasonable the capture and storage of emissions that otherwise would be neutral. Hence, the negative emissions should be economically valorized. This valorization could be via the sale of CO_2 credits (emission trading) or indirectly via subsidies. However, regulation must define the way in which negative emissions are accounted for and if merely those emissions that are actually sequestrated could be taken into account or not. For example, in a thermochemical biorefinery with BECCS, the assessment of sustainability could give different cases (under the framework of European regulation):

A. The process before BECCS incorporation achieves a lower saving in GHG emissions than that required by the regulation. The incorporation of BECCS allows the biorefinery to just achieve the regulation. In this case, the sequestrated CO_2 cannot be considered as negative emissions that could be economically valorized.
B. The process before BECCS incorporation achieves a lower saving in GHG emissions and the incorporation of BECCS allows the biorefinery to achieve a saving larger than that regulated. In this case, the sequestrated CO_2 cannot be completely counted as negative emissions that could be economically valorized. Only the fraction of CO_2 that is an extra saving with respect to the regulation could be valorized (extra-avoided emissions).
C. The process before BECCS incorporation achieves the same saving in GHG emissions as that required by the regulation. In this case, the sequestrated CO_2 counts as negative emissions that could be economically valorized.
D. The process before BECCS incorporation achieves a larger saving in GHG emissions than that required by the regulation. In this case, there is an extra saving that does not depends on the sequestrated CO_2, which again counts as negative emissions that could be economically valorized. Hence, it would be possible to sell a larger amount of CO_2 credits than those from BECCS incorporation (negative emissions). If it were not possible, the whole extra-avoided emissions would not be valorized, penalizing the thermochemical biorefinery.

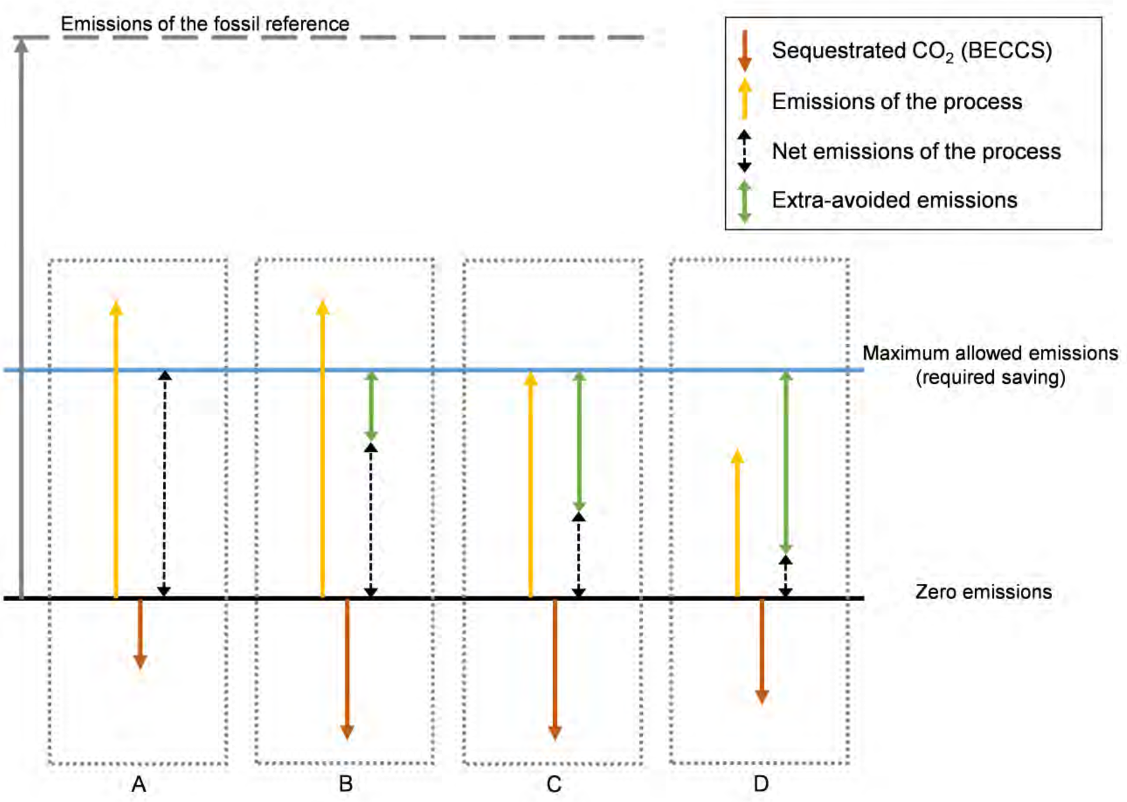

Figure 4. Different cases when BECCS is incorporated into thermochemical biorefineries.

4.3. Economic assessment

In the economic assessment of proposed concepts of a thermochemical biorefinery, there are significant uncertainties that make the resulting profitability doubtful. Examples of such uncertainties are the cost of the processing technologies (gasification, syngas cleaning), the price of biomass (feedstock) and the evolution of the market of bio-products and their regulation. The case of thermochemical biorefineries is somehow simpler than biochemical biorefineries, since the potential bio-products are those currently used or proved substitutes for fossil equivalents. Nonetheless, the profitability of thermochemical biorefineries requires, due to the larger scale of the plant, a larger investment. These uncertainties are not considered in the thesis, which assumes that the eruption of bioenergy has no impact on the market, which could only be accurate for the first commercial plants.

In the thesis, two different methodologies have been considered for the economic assessment: a general methodology for most of the cases (the economic methodology used by BEGUS) and a methodology for the cases designed in collaboration with KIT (the economic methodology used in the bioliq® project).

4.3.1. General methodology

For the economic assessment, it is assumed that the realization of the project (plant) is at medium term, assuming the required development of the technology (e.g. gasification, syngas cleaning, catalyst development). This general methodology is that followed by NREL (National Renewable Energy Laboratory, USA) and also by the BEGUS group for the assessment of thermochemical biorefineries without multiproduction and it has been modified for the assessment of multiproduction plants. The biomass price assumed in the methodology is 2.6 €/GJ.

For single production plants (Papers 2 and 3), the minimum selling price of the product has been calculated by imposing an internal rate of return (IRR) of 10% (considered the minimum acceptable for the investment in a thermochemical biorefinery). The results from the process simulations were used to estimate capital and operating costs. Purchase costs for equipment (PEC) are taken from published BTL/G studies and vendor quotes. First, the purchase costs are scaled and the effect of inflation is corrected using the CEPCI (Chemical Engineering Plant Cost Index) index. Then, the installed equipment cost is calculated by multiplying the purchase cost by an installation factor. Thus, the total installed cost (TIC) is calculated by adding up the cost of the individual equipment. The indirect costs are estimated as percentages of TIC as shown in Table 2. The expected accuracy of the estimate is ±30%. Finally, the operating costs are calculated according to Table 3. Fixed operating costs are calculated as a percentage of TIC while variable operating costs are calculated based on the cost of the consumables. Once the capital and operating costs are calculated, the minimum selling price of the product is calculated as the product price that makes the net present value of the project zero (with an IRR of 10%). The economic parameters used for the discounted cash flow analysis are shown in Table 4.

For the economic assessment of thermochemical biorefineries with multiproduction, the presence of more than one main product forces the search of an alternative for the calculation of the minimum selling price (once the internal rate of return is fixed). The problem arises from multiproduction, which gives as many variables for economic assessment as co-products the plant has. The proposed modification of economic methodology is that the IRR of each concept (plant) is calculated by setting the market price of products in the DCFA (discounted cash flow analysis), i.e. the commercial price of co-products and services are fixed for the calculation. In this case, the IRR is the result of the economic assessment.

Table 2. Cost factors for estimating direct and indirect costs as a percentage of purchase cost equipment (PEC) and total installed cost (TIC), respectively.

Direct Cost	% PEC
Purchase equipment installation	39
Instrumentation and control	26
Piping	31
Electrical systems	10
Building (including services)	29
Yard improvements	12
Total direct costs	147
Indirect Costs	**% TIC**
Engineering design and procurement	7.9
Contractor Management and control	2.2
Capital spares and other costs	2.0
Operator training	1.0
Start up assistance	1.0
EPC constructor contingency	15.0
Total indirect costs	29.1

Table 3. Data for calculating the fixed operating costs.

Fixed operating costs	% TIC
Labor	1.56
Maintenance	1.50
General expenses	3.07
Management and operation services	0.44
Cost of Goods Sold- Marketing, Logistics and others	1.32
Insurance	0.50
Total	8.39

Table 4. Economic assumptions for discounted cash flow analysis.

Parameter	Value
Operating hours	8000
Rate of return	10%
Debt/Equity	0/100%
Plant life	20 years
Depreciation (Linear)	10 years
Salvage value	0 M USD
Construction period	1 year
Income tax	30%
Working capital	1-month operating costs
Land	6% TIC

Working capital and cost of land are recovered at the end of plant life.

4.3.2. Methodology for the cases in collaboration with KIT (bioliq®)

This methodology only applies to the assessment of plants within the bioliq® concept (Paper 5), where current data have been used for the economic assessment. The biomass price is 3.8 €/GJ according to the estimations of KIT.

Based on the operating data for the main equipment of the biorefinery, the total capital investment can be estimated using ratio factors for direct and indirect capital investment. Table 5 summarizes the assumed ratio factors for the control system, piping and further direct capital investments as well as the ratio factor for indirect capital investments, such as engineering or legal expenses. The ratio factors are selected according to process conditions, design complexity and required materials in this study. The applied ratio factor method implies uncertainties of ±30%.

For the economic assessment of thermochemical biorefineries with multiproduction, a different alternative has been evaluated. In this case, the relationship between specific production costs is assumed to remain the same as in current market prices. Therefore, the IRR has been fixed by calculating the percentage change over the market prices of co-products and services.

4.3.3. Subsidies and economic valorization of the extra saving of GHG emissions

The promotion of thermochemical biorefineries corresponds to the public sector and a global legal framework should be given in order to have compatible regulations (e.g. EU and USA). For example, the use of biofuels may be promoted via subsidies (tax exceptions, bonus) or imposing a general quota for their use. However, these solutions refer to the energy sector. For bio-chemicals, the imposition of an environmental tax on final products (e.g. plastics) could be a solution. The economic valorization of the extra-avoided emissions (extra saving) in biorefineries is a proposal that could homogenize the treatment of all kind of biorefineries including bio-chemical ones. However, current regulations do not allow it. If it were not possible in the future regulation, an extra-saving in GHG emissions could always be translated into the allowance for coal or natural gas co-feeding in the biorefinery to reach the regulated saving, since it does not require of a change in regulations [*see Papers 4 and 7 for further discussion*].

Table 5. Ratio factors for direct and indirect capital investment in the concepts using the bioliq® concept.

Direct investments	**%**
Investment for installed equipment	100
Instrumentation and control	24
Piping	46
Electrical systems	8
Buildings	12
Yard improvements	7
Service facilities	48
Total direct investment	245
Indirect investments	**%**
Engineering and supervision	22
Construction expenses	28
Legal expenses	3
Contractor's fee	15
Contingency	30
Total indirect investment	98
Fixed Capital Investment	343

Table 6. Summary of economic assumptions in the concepts using the bioliq® scenario.

Parameters for investment dependent costs		
Capacity factor	%	80
Expected lifetime	Years	20
Depreciation (no scrap value)	linear	-
Interest rate	%	7.0
Working capital	% of fixed capital investment	5.0
Maintenance costs (average)	% of fixed capital investment	3.0–3.6
Insurance & taxes	% of fixed capital investment	2.0

5. Results and discussion

5.1. Description of the concepts

In the thesis, 20 different concepts of a thermochemical biorefinery have been designed and assessed. The processes differ in their process configuration (gasification and syngas conditioning technologies, and process integration) and in the selected mix of products. The considered products are shown in Table 7, where it can be seen that there is frequently more than one use for the same product, which is an advantage.

Table 7. Summary of considered products and services in the assessed concepts of a thermochemical biorefinery.

Product	**Use**			
	Transport fuel	**Fuel for heating**	**Commodity**	**Chemical (high-value)**
Ethanol	Yes (substitute for gasoline)	No	Yes (e.g. for ethylene or bio-butanol synthesis)	No
DME	Yes (substitute for diesel)	Yes (substitute for LPG)	Yes (e.g. substitute for naphtha)	No
Methyl acetate	No	No	No	Yes (solvent, plastic precursor and other uses)
H_2	Yes [a] (potential use)	No	Yes	No
Ethylene	No	No	Yes (e.g. for plastic production)	No
Propylene	No	No	Yes (e.g. for plastic production)	No
Synthetic gasoline	Yes (replaces gasoline)	No	No	No
Electricity (service)	-	-	-	-

[a] The use of H_2 for potential applications like hydrogen for transportation and the use of hydrogen cell are not considered.

The concepts of a thermochemical biorefinery that have been proposed in this thesis are summarized in Table 8. There are 20 concepts in total, where DME is the common platform chemical in most cases (17) and ethanol in the rest (3). The concepts of a thermochemical biorefinery with multiproduction amount to 14, co-producing biofuels, bio-chemicals and electricity.

The *i-Ethanol* concept was the first designed and assessed concept of the thesis. It uses DME as an intermediate (platform chemical) for the synthesis of ethanol from biomass-derived syngas via the DME hydrocarbonylation route (an indirect route). In this concept, an i-CFB gasifier was selected for the gasification of 500 MW of poplar chips feedstock (HHV basis). The single product was ethanol and the plant was designed in order to be "electric energy neutral".

The *Ethylene A-D* concepts were designed in order to assess the conversion of bioethanol into a more valuable product (ethylene). They are not focused on multiproduction; and contrary to the other concepts, they use ethanol as a platform chemical. They differ in the origin of the bioethanol, i.e. the *A* concept uses commercial bioethanol (3 alternatives: bioethanol from the USA, Brazil and the EU); the *B* concept analyzes the potential use of 2nd generation bioethanol (from enzymatic hydrolysis and fermentation of syngas); the *C* concept analyzes the installation of a dehydration plant in a thermochemical biorefinery producing ethanol via direct synthesis; and the *D* concept analyzes the same idea but in the biorefinery of the *i-Ethanol* concept (indirect synthesis of ethanol).

The *SR*, *ATR* and *TR* concepts were designed as multiproduction plants based on the DME hydrocarbonylation and DME carbonylation routes. The plant capacity of these concepts is also 500 MW of biomass input (HHV basis), all using an i-CFB gasifier. They differ in the kind of cleaning and conditioning of the raw syngas (the *SR* concepts use a steam reformer, the *ATR* use an autothermal reformer, and the *TR* use a tar reformer after the gasifier) and the selected mix of products. In the *TR* concepts, the incorporation of BECCS is analyzed, since they require the removal of CO_2. Therefore, in these concepts, only the compression of CO_2 is necessary for the transport and sequestration of BECCS.

The *Gasoline*, *Olefins* and *Gasoline & Ethylene* concepts were designed according to the bioliq® project in collaboration with KIT, using their assumptions for plant capacity (1175 MW_{th}, HHV basis) and biomass feedstock (straw). These concepts use DME as a platform chemical for the production of synthetic gasoline (*Gasoline*) and olefins (*Olefins*), as thermochemical biorefineries without multiproduction. In order to analyze the potential integration of both cases (i.e. multiproduction plant), the *Gasoline & Ethylene* concept combines the DME-to-gasoline and DME-to-olefins routes.

Table 8. Concepts of thermochemical biorefinery studied in the thesis.

Concept	Feedstock	Gasifier	Platform chemical	BECCS	Description	Products	Multiproduction	Paper
i-Ethanol	Poplar chips [500 MW, HHV]	i-CFB	DME	No	Indirect synthesis of ethanol via the DME hydrocarbonylation route	Ethanol	No	2
Ethylene A (case study 1)[a]	1st generation bioethanol [148 – 495 MW, HHV]	-	Ethanol	No	Dehydration of commercial ethanol (USA, Brazil, EU)	Ethylene	No	3
Ethylene B (case study 2)[a]	2nd generation bioethanol [297 – 990 MW, HHV]	-	Ethanol	No	Dehydration of ethanol from enzymatic hydrolysis or syngas fermentation	Ethylene	No	3
Ethylene C (case study 3)[a]	Poplar chips [500 MW, HHV]	EF	Ethanol	No	Dehydration of ethanol from direct synthesis (thermochemical processing)	Ethylene	No	3
Ethylene D (case study 4)[a]	Bioethanol [199 MW, HHV]	-	DME / Ethanol	No	Dehydration of ethanol from concept i-Ethanol	Ethylene	No	3
SR-01	Poplar chips [500 MW, HHV]	i-CFB	DME	No	DME hydrocarbonylation route, using a steam reformer (conditioning)	Ethanol and electricity	Yes	5
SR-02		i-CFB	DME	No		Ethanol, DME and electricity	Yes	5
SR-03		i-CFB	DME	No	DME carbonylation route, using a steam reformer (conditioning)	Methyl acetate, DME and electricity	Yes	5

ATR-01	Poplar chips [500 MW, HHV]	i-CFB	DME	No	DME hydrocarbonylation route, using an autothermal reformer (conditioning)	Ethanol and electricity	Yes	5
ATR-02		i-CFB	DME	No		Ethanol, DME and electricity	Yes	5
ATR-03		i-CFB	DME	No	DME carbonylation route, using an autothermal reformer (conditioning)	Methyl acetate, DME and electricity	Yes	5
TR-01		i-CFB	DME	Yes	DME hydrocarbonylation route, using a tar reformer (conditioning)	Ethanol and electricity	Yes	5 and 7
TR-02		i-CFB	DME	Yes		Ethanol, H_2 and electricity	Yes	5 and 7
TR-03		i-CFB	DME	Yes		Ethanol, DME and electricity	Yes	5 and 7
TR-04		i-CFB	DME	Yes		Ethanol, H_2 and DME	Yes	5 and 7
TR-05		i-CFB	DME	Yes	DME carbonylation route, using a tar reformer (conditioning)	Methyl acetate, H_2 and DME	Yes	5 and 7
TR-06		i-CFB	DME	Yes		Methyl acetate, DME and electricity	Yes	5 and 7

Gasoline	Straw [1175 MW, HHV]	EF	DME	Yes	Synthesis of gasoline via the DME-to-gasoline route	Synthetic gasoline	No	6
Olefins (case study 5) [a]		EF	DME	Yes	Synthesis of olefins via the DME-to-olefins route	Olefins (ethylene and propylene)	Yes	3 and 6
Gasoline & Ethylene		EF	DME	Yes	Synthesis of ethylene via the DME-to-olefins route and synthesis of gasoline via the olefins-to-gasoline route	Synthetic gasoline and ethylene	Yes	6

[a] The names in brackets are the corresponding names of the concepts in Paper 3.

5.2. Material, energy and economic results

Table 9 shows the results of the material and energy balances of the assessed concepts of a thermochemical biorefinery. These concepts achieve an average energy efficiency of 40%[§]. However, the average carbon efficiency is about 25 % (carbon content of the biomass that is in the products) and about 20% in the concepts that have H_2 and electricity as co-products. The highest energy efficiency corresponds to the *TR-02* concept (thermochemical biorefinery with multiproduction), where ethanol, DME and electricity are co-produced (50%, HHV basis). The lowest energy efficiency corresponds to the *Ethylene C* concept[**]. In the case of the i-Ethanol concept, the biomass-to-ethanol efficiency is 369 L per tonne of dry biomass.

The capital investment of a plant without multiproduction, i.e. the *i-Ethanol* concept, is about 1.1 M€$_{2011}$/MW$_{\text{products}}$ using the economic methodology of BEGUS. For multiproduction plants, i.e. the *SR*, *ATR* and *TR* concepts, the ratio ranges from 1.7 to 2.6 M€$_{2011}$/MW$_{\text{products}}$. Therefore, there is an increase in the capital investment in multiproduction plants[††]. The operating cost of the plant is lower than in single product biorefineries (300–400 k€/MW$_{\text{products}}$ vs. 435 k€/MW$_{\text{products}}$). Hence, multiproduction balances the larger investment by a reduction of the operating cost, which is the result of the better energy and material integration of these kind of thermochemical biorefineries.

In the case of *Ethylene A* and *B* concepts, the production of the platform chemical (ethanol) is not included and the resulting investment is low (23–45 k€$_{2011}$/MW$_{\text{products}}$). Nevertheless, the operating costs in these concepts are higher (about 500 k€/MW$_{\text{products}}$) and, therefore, the profitability of the plant depends on the price of the bioethanol feedstock. Otherwise, the *Ethylene C* and *D* concepts do consider the whole processing in the biorefinery facility; and their ratio of capital investment (3.8 and 1.6 M€$_{2011}$/MW$_{\text{products}}$) and operating cost (740 and 470 k€/MW$_{\text{products}}$) are slightly higher than those of the *i-Ethanol* concept. The increase of both investment and operating costs of *C* and *D* concepts is due to the increased equipment in the biorefinery (dehydration of ethanol) and a poor energy and material integration (typical of single product plants).

For the concepts assessed in collaboration with KIT, the economic results are different to those previously commented upon. The ratio of capital investment is about 2.1 M€$_{2011}$/MW$_{\text{products}}$, and the ratio for the operating cost about 825 k€/MW$_{\text{products}}$ (higher because of the hardest economic scenario for this concepts, see section 4.3.2.). These results seems not to depend on the kind of

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[§] This is not a low value of energy efficiency, since the largest energy losses are due to the production of the syngas (gasification) [*more details and the definitions of efficiency are given in Paper 4*].

[**] This low efficiency is because of the low efficiency in the production of ethanol via direct synthesis from syngas (the energy efficiency to ethanol is of 24%) and not because of the processing of the ethanol [*see Paper 3 for further details*].

[††] However, these results are lower than the investment cost of a power plant (biomass gasification plus a motor engine) using biomass, which is of 2.5–3.0 M€/MW$_{\text{electricity}}$.

biorefinery (with or without multiproduction). However, regarding the design of each concept, the benefit of multiproduction can be found. The *Gasoline & Ethylene* concept produces gasoline at a lower cost than in the Gasoline concept, despite having higher investment and operating costs. This is because of the integration of gasoline and olefin production.

Regarding the concepts in which the selling price of the product(s) is calculated (see section 4.3.), the *i-Ethanol* concept is able to produce ethanol at a similar cost to Brazilian ethanol and be profitable and lower than the price of the direct route[‡‡]. Furthermore, the *Ethylene A* concept can sell competitive ethylene for all current ethanol feedstock except for European ethanol. The use of 2nd generation ethanol via enzymatic hydrolysis is not profitable for ethylene production (*Ethylene B* concept). However, the use of ethanol from the *i-Ethanol* concept does allow the same profitability than as when using Brazilian ethanol (*Ethylene D* concept). For the concepts assessed in collaboration with KIT (*Gasoline*, *Olefins*, *Gasoline & Ethylene*), however, the selling price of products is remarkably expensive compared to the commercial prices. Regarding the concepts in which the IRR is calculated, the differences between the best (ATR-03, TR-05, SR-03) and worst case (TR-03, TR-01, TR-04) resulting IRRs are due to the co-production or not of a high-value product, i.e. methyl acetate. The concepts achieving the best profitability always produce methyl acetate, which is the selected high-value product.

Figure 5 shows the commercial prices used in the assessments along with the resulting minimum selling prices regarding the concept. It can be seen that methyl acetate has the highest commercial price (65 €/GJ) and it is twice the price of ethanol, ethylene and gasoline. The commercial price of ethanol [*see Paper 3*] depends largely on the origin of the ethanol and the consequent uncertainty is transmitted to the results of the ethylene price, which has more than a 70% difference regarding the origin of the ethanol. H_2 is the product with the lowest commercial price and it there are also problems with its distribution. However, its potential uses (e.g. as transportation fuel) and the potential integration with other facilities (e.g. ammonia production, urea, etc.) could make it of interest.

Comparing the results with the estimation of the future development of the bio-energy sector, the production of ethanol via the DME hydrocarbonylation route (*i-Ethanol*) is 16.4 €/GJ, which lies in the scenario estimated by Chalmers University for biofuels (between 10 and 20 €/GJ) [2]. However, in the case of the concepts in collaboration with KIT, the resulting selling price for gasoline is quite high (36.8 $/GJ) and above the estimated maximum by Chalmers University.

[‡‡] The techno-economic assessment of the direct route by BEGUS results in a minimum selling price of ethanol of about 0.7 $/L, which is larger than the equivalent minimum selling price of the indirect route (*i-Ethanol*).

Table 9. Summary of material and energy results (production) of the assessed concepts of thermochemical biorefinery.

Concept	**Ethanol (ML/year)**	**DME (kt/year)**	**Methyl acetate (kt/year)**	**H_2 (kt/year)**	**Synthetic gasoline (ML/year)**	**Ethylene (kt/year)**	**Propylene (kt/year)**	**Electricity (MW)**	**Others (kt/year)**	**Energy efficiency[a] (%)**
i-Ethanol	263	-	-	-	-	-	-	-	-	46
Ethylene A	-	-	-	-	-	70 – 273	-	-	-	82[b]
Ethylene B	-	-	-	-	-	147 – 477	-	-	-	82[b]
Ethylene C	-	-	-	-	-	63	-	-	Methanol: 40 Propanol: 16	31
Ethylene D	-	-	-	-	-	105	-	-	-	40
SR-01	221	-	-	-	-	-	-	23	-	43
SR-02	221	16	-	-	-	-	-	2	-	42
SR-03	-	107	74	-	-	-	-	24	-	39
ATR-01	218	-	-	-	-	-	-	7	-	39
ATR-02	216	5	-	-	-	-	-	8	-	40
ATR-03	-	121	74	-	-	-	-	9	-	39
TR-01	181	-	-	-	-	-	-	61	-	44
TR-02	181	-	-	16	-	-	-	18	-	50
TR-03	128	29	-	-	-	-	-	32	-	35
TR-04	128	29	-	16	-	-	-	-	-	43
TR-05	-	107	71	16	-	-	-	-	-	49
TR-06	-	107	71	-	-	-	-	42	-	42
Gasoline	-	-	-	-	210	-	-	57	-	38
Olefins	-	-	-	-	-	116	100	-	LPG: 42	41
Gasoline & Ethylene	-	-	-	-	128	116	-	-	-	39

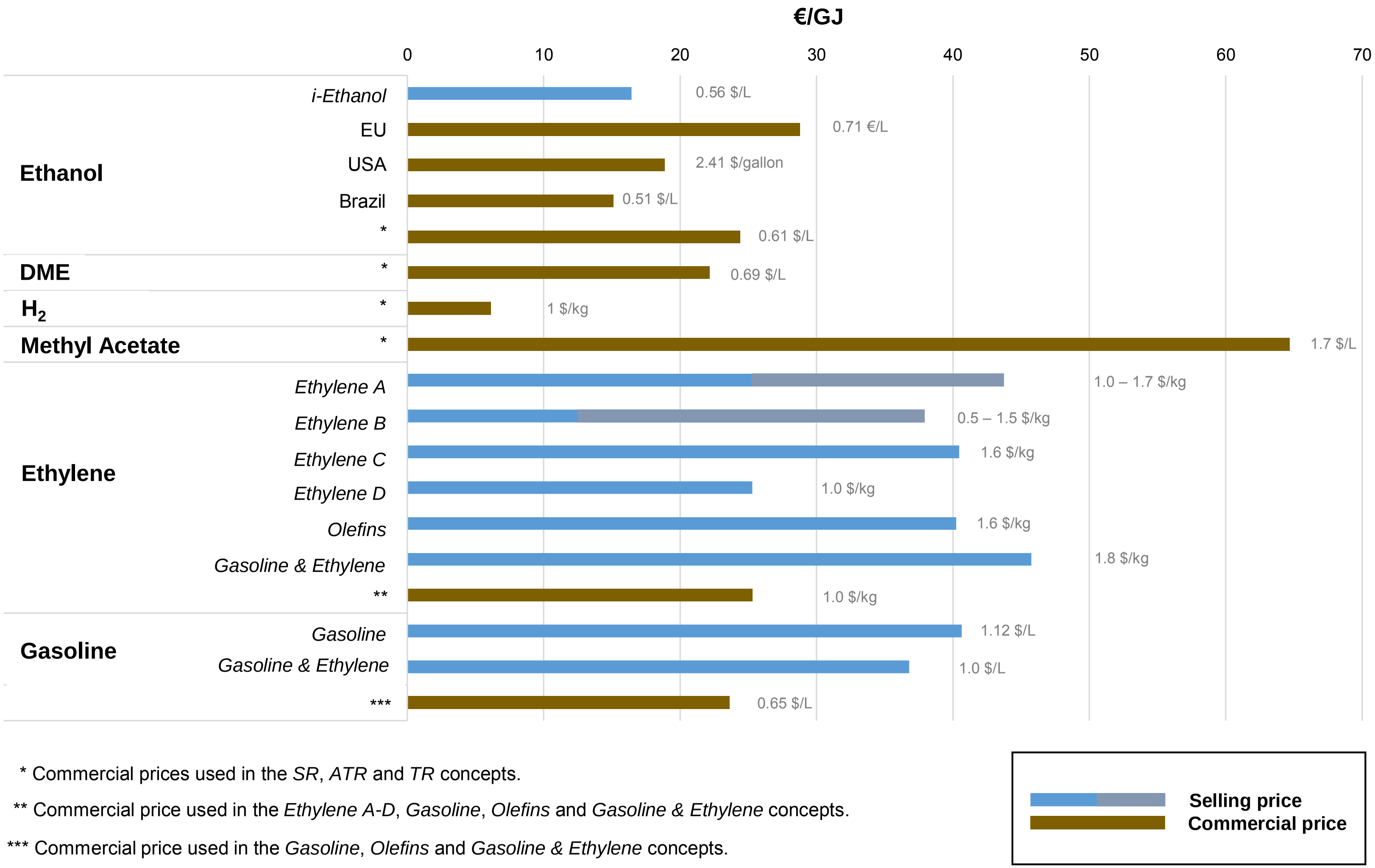
[a] The energy efficiency corresponds to $\eta_{th,\ total}$ [*see Paper 4 for further details of the definition of energy efficiency in thermochemical biorefineries with multiproduction*].

Table 10. Summary of economic results of the assessed concepts of a thermochemical biorefinery.

Concept	Capital Investment	Operating cost	IRR (%)	Selling price
i-Ethanol	333 M$\$_{2010}$	100 M$\$_{2010}$/year	10	0.56 $/L (0.42 €/L)
Ethylene A[a]	6.2 – 13.6 M€$_{2011}$	77 – 257 66 – 219 115 – 383 (M€$_{2011}$/year)	10	USA: 1.2 €/t Brazil: 1.0 €/t EU: 1.7 €/t
Ethylene B[a]	9.8 – 21.3 M€$_{2011}$	191 – 713 67 – 224 (M€$_{2011}$/year)	10	Enz. hydrolysis: 1.5 €/kg Syngas ferment.: 0.5 €/kg
Ethylene C	447 M€$_{2011}$	87 M€$_{2011}$/year	10	1.6 €/t
Ethylene D	342 M€$_{2011}$	99 M€$_{2011}$/year	10	1.0 €/t
SR-01	422 M$\$_{2010}$	79 M$\$_{2010}$/year	10	Commercial prices [b]
SR-02	407 M$\$_{2010}$	79 M$\$_{2010}$/year	12	
SR-03	497 M$\$_{2010}$	83 M$\$_{2010}$/year	23	
ATR-01	356 M$\$_{2010}$	87 M$\$_{2010}$/year	9	
ATR-02	356 M$\$_{2010}$	88 M$\$_{2010}$/year	10	
ATR-03	407 M$\$_{2010}$	90 M$\$_{2010}$/year	29	
TR-01	491 M$\$_{2010}$	83 M$\$_{2010}$/year	5	
TR-02	431 M$\$_{2010}$	80 M$\$_{2010}$/year	8	
TR-03	501 M$\$_{2010}$	84 M$\$_{2010}$/year	1	
TR-04	434 M$\$_{2010}$	81 M$\$_{2010}$/year	5	
TR-05	486 M$\$_{2010}$	83 M$\$_{2010}$/year	24	
TR-06	553 M$\$_{2010}$	87 M$\$_{2010}$/year	20	
Gasoline	964 M€$_{2011}$	404 M€$_{2011}$/year	7	1.12 €/L
Olefins	1026 M€$_{2011}$	424 M€$_{2011}$/year	7	Ethylene: 1.59 €/kg Propylene: 1.56 €/kg
Gasoline & Ethylene	1025 M€$_{2011}$	425 M€$_{2011}$/year	7	Gasoline: 1.03 €/L Ethylene: 1809 €/t

[a] The values shown for these concepts refer only to the dehydration plant. The production of ethanol in these concepts is not included in the assessment.

[b] See Figure 5.



* Commercial prices used in the *SR*, *ATR* and *TR* concepts.

** Commercial price used in the *Ethylene A-D*, *Gasoline*, *Olefins* and *Gasoline & Ethylene* concepts.

*** Commercial price used in the *Gasoline*, *Olefins* and *Gasoline & Ethylene* concepts.

Figure 5. Comparison of sale and commercial prices for the different concepts of a thermochemical biorefinery assessed in the thesis. The values in gray are the corresponding values in their assessment. They are converted into €/GJ assuming a conversion $/€ factor of 1.35.

5.3. CO_2 emissions, incorporation of BECCS and sustainability

Table 11 presents the CO_2 emissions (limited to the biorefinery) of the proposed concepts of a thermochemical biorefinery. These emissions are classified into two groups: neutral emissions due to the combustion of renewable carbon and total emissions in the plant (biorefinery), the difference being the emissions due to the use of fossil fuels, consumables, etc. In some concepts, CO_2 has to be removed (capture) and the removed CO_2 could be sequestrated (incorporation of BECCS). For the cases where there is a capture unit, the amount of CO_2 is expressed in t/h along with the resulting sequestration costs (including transport and sequestration) for the CO_2. The cost of the sequestration of CO_2 in the assessed concepts, which includes all steps from the capture to the final storage, are lower than the equivalent of power plants (about 100 – 200 €/t) [8]. This is an important benefit, since BECCS does not merely give a negative emission to the plant, but it can be afforded at lower prices than conventional power plants.

The assessment of sustainability has been conducted only for the *SR*, *ATR* and *TR* concepts, which are the concepts with multiproduction and which achieve the best profitability. The extra-avoided emissions (considered the extra saving above the minimum saving regulated by the European Directive and expressed as the amount of CO_2 equivalent per MJ of products) are presented in Figure 5. The results show that the production of bioproducts with a final use as chemicals gives the highest extra-avoided emissions. Moreover, it can be seen that all the concepts achieve the minimum saving of the European regulation. The sale of extra-avoided emissions (extra revenue) and the co-feeding of coal (reduction of operating cost) are considered the potential ways for the valorization of the extra saving and result in an enhancement of profitability, which is analyzed.

If the extra saving is translated into an economic benefit, there will be an increase in the revenue of the plant (case of sale of CO_2 credits) or a reduction of the operating cost (case of co-feeding of fossil fuels in the biorefinery). Both alternatives have been analyzed and co-feeding would be favored if the price of the CO_2 credits were below 20 €/t [*see Paper 7 for further details*].

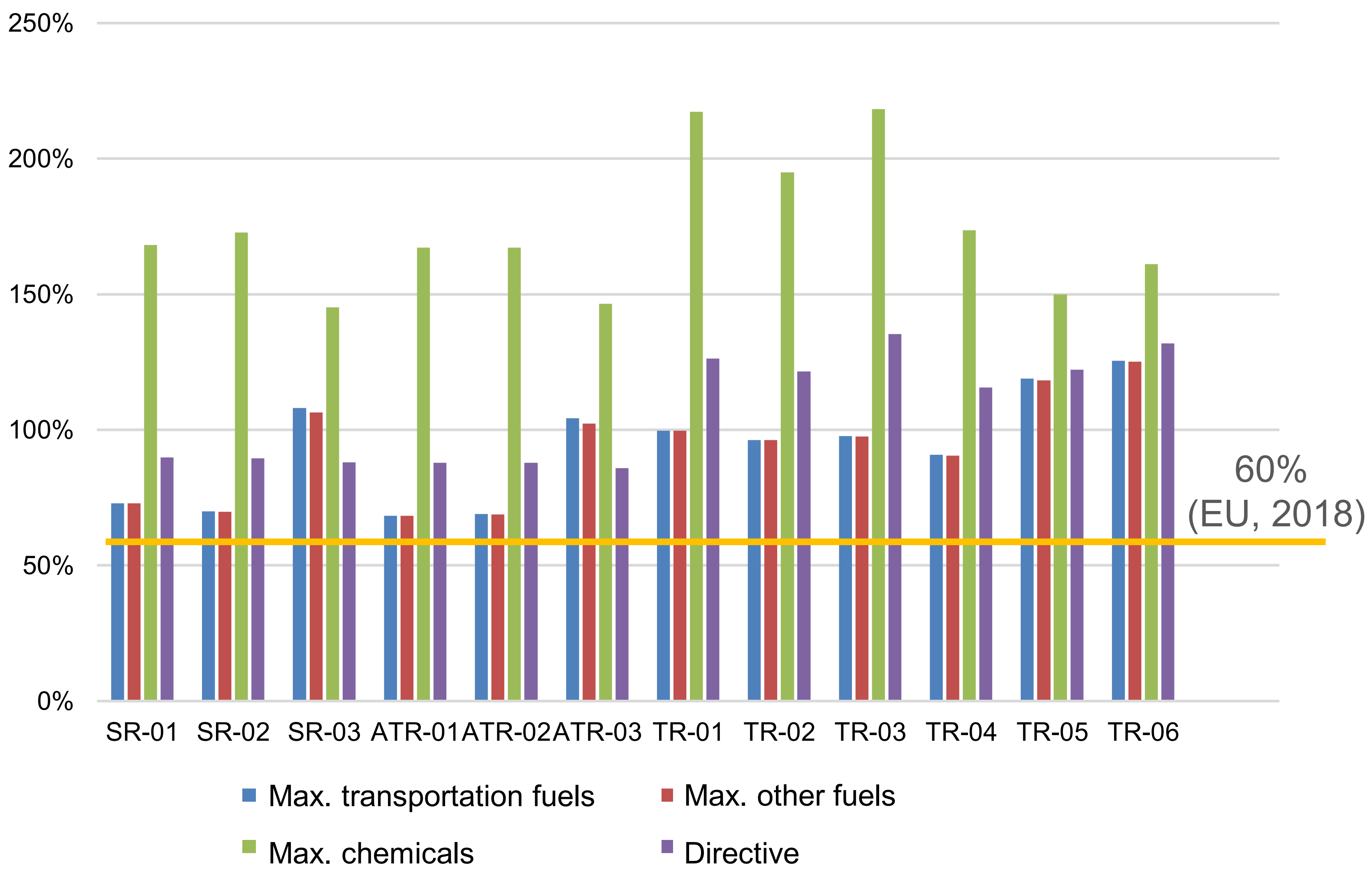
Table 11. Summary of CO_2 emissions and incorporation of BECCS into the concepts of a thermochemical biorefinery[a].

Concept	**Neutral CO_2 emissions (t/h)**	**Total CO_2 emissions (t/h)**	**CO_2 available for sequestration (t/h)[b]**	**CO_2 sequestration costs (€/t)**
i-Ethanol	113	113	31	30
Ethylene A[c]	59	-	55	26
Ethylene B[c]	127 – 518	559	109	26
Ethylene C	136	139	101	33
Ethylene D	115	120	31	30
SR-01	141	141	0	-
SR-02	136	136	0	-
SR-03	140	140	0	-
ATR-01	141	141	0	-
ATR-02	140	140	0	-
ATR-03	137	137	0	-
TR-01	125	125	23	22
TR-02	135	135	23	22
TR-03	128	128	23	22
TR-04	128	128	23	22
TR-05	117	117	23	24
TR-06	118	118	23	24
Gasoline	319	319	88	39
Olefins	295	295	125	39
Gasoline & Ethylene	303	303	125	39

[a] The presented value refer only to the emissions of CO_2 in the plant (biorefinery).

[b] The CO_2 that is already capture in the plant and therefore, it can be conditioned for sequestration.

[c] In these cases the ethanol production, as well as the potential capture of CO_2 is not included in the system boundaries of this study. The given values outside system boundaries are estimated from the literature and shown in italics.


250%
200%
150%
100%
50%
0%
SR-01
SR-02
SR-03
ATR-01
ATR-02
ATR-03
TR-01
TR-02
TR-03
TR-04
TR-05
TR-06
60%
(EU, 2018)
Max. transportation fuels
Max. other fuels
Max. chemicals
Directive

6. Conclusions and recommendations for further work

This thesis has investigated the conceptual design and assessment of thermochemical biorefineries with special attention to those using DME as a platform chemical for the production of transportation fuels (ethanol, DME and synthetic gasoline), fuels for heating (DME) and chemicals (commodities: H_2, DME, ethylene and propylene, and of high-value: methyl acetate).

The review of chemical routes via a platform chemical has demonstrated that there is a great potential for the design of new concepts of a thermochemical biorefinery and new routes could still be used if new platform chemicals were considered (**Paper 1**). The fact that the reviewed routes could be applied to a fossil feedstock, e.g. coal and natural gas, is a natural consequence of the concept of a thermochemical biorefinery and an advantage, since both the technology and the know-how from the processing of fossil feedstocks can be adapted and integrated in a thermochemical biorefinery. The use of an intermediate (platform chemical) enhances productivity and gives better results compared to direct synthesis from syngas despite the complexity of the plant (**Papers 2** and **3**). The routes via a platform chemical are versatile and can be combined for the co-production of different sorts of products and services: biofuels, bio-chemicals (commodities and high-value products), materials, electricity and heat (**Papers 1** and **4**). Multiproduction biorefineries benefit from the co-production of low-value high-volume (e.g. transportation fuel, commodities) with high-value low-volume (e.g. chemicals for the organic industry, high-value materials) products. Thermochemical biorefineries with multiproduction benefit from economies of scale for the production of a high-value chemical; therefore, the concepts co-producing a high-value product (methyl acetate) achieve the best profitability (**Paper 5**). The proposed modification of European regulations on sustainability has introduced bio-chemicals into the assessment. The introduction of bio-chemicals brings uncertainties surrounding the potential benefits of partial storage of their carbon content; however, the results are still favorable even if this storage were neglected. Sustainability is achieved in all assessed concepts and there is an extra saving that should be valorized in order to promote the larger saving of GHG emissions in this kind of plant (**Paper 7**).

Further research should continue into the design and assessment of new concepts of thermochemical biorefineries using a platform chemical. Despite the inherent complexity of this kind of plant, similar profitability and energetic efficiency to other BTL/G processes is achieved. The use of biomass as feedstock for the petrochemical industry could be crucial for the future of biomass and for a large increase in GHG saving in the coming years. However, current regulations on bio-chemicals are scarce and future regulations on bioenergy should not disregard the potential synergies of the multiproduction of fuels, chemicals and services.

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Paper 1

Potential Routes for Thermochemical Biorefineries

This paper presents a critical review of chemical routes via a platform chemical (carbochemistry) that have a potential in the design of thermochemical biorefineries. It has been published as paper in 2013[*].

1. Introduction

Currently, the uses of biomass as a renewable source account for the production of 1st generation ethanol and FAME (fatty acid methyl ester) biodiesel, in addition to the generation of heat and power. Nonetheless, there is controversy over the use of food-competitive biomass for the production of fuels. The low mass yield of 1st generation processes often makes them unprofitable at current biomass price. Furthermore, expected future regulation of biofuels in the EU could exclude them or impose strong limitations in order to fulfill the sustainability criterion [1]. In response to that, 2nd generation processes have been proposed and several demonstration projects, based on the biochemical conversion of lignocellulosic biomass, are reported for the production of non-food-competitive bioethanol [2,3]. In a prior stage of development are the BTL/G (biomass to liquids/gases) processes, focusing on the thermochemical conversion of biomass into synthesis gas (syngas) or pyrolysis oil, which is then converted into products.

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[*] Haro P, Ollero P, Villanueva Perales AL, Vidal-Barrero F. Potential routes for Thermochemical *Biorefineries. Biofuels, Bioproducts and Biorefining*. 2013;7(5):551-72. DOI: 10.1002/bbb.1409

Nomenclature

BETE: bioethanol-to-ethylene
BTL/G: biomass-to-liquid/gas
CCS: carbon capture and storage
CFB: circulating fluidized bed
DME: dimethyl ether
EF: entrained flow
GHG: greenhouse gas
LCA: life cycle assessment
LPMEOH: liquid-phase methanol
MTG: methanol-to-gasoline
MTO: methanol-to-olefins
MSW: municipal solid waste
WGS: water gas shift

Research on BTL/G processes is limited to various types of potential bio-products [4-8], i.e. Fischer-Tropsch (FT) diesel [9-16], ethanol [17-24], methanol [14,15,25-31], DME [16,29,30,32-36], H_2 [25,26,30,37,38], synthetic natural gas (SNG) [11,39-43] and urea [14,15]. Each of these processes has focused on the production of a single fuel, either with or without the co-production of heat/electricity. Rather than producing a single product, a more interesting option is a multi-product plant, either by combining two or more known BTL/G processes, or based on a chemical intermediate (platform chemical) [14,44].

In a thermochemical biorefinery fuels, chemicals and power are co-produced. A first technoeconomic assessment of such a multi-product plant (thermochemical biorefinery) based on a platform chemical has shown there are important benefits compared to studied BLT/G plants, i.e. greater profitability due to the co-production of high value products, the possibility of overcoming (e.g. in ethanol synthesis) the limitations of product selectivity and a better energy and material integration [44].

Within 2nd generation processes, different concepts of biorefineries are subject of special attention nowadays. Despite the uncertain classification of biorefineries[†], a thermochemical biorefinery involves (in the opinion of the authors) the processing of biomass and carbon-based waste, i.e. organic fraction of municipal solid waste (MSW), to generate (simultaneously) products and services covering fuels, chemicals, heat and electricity from syngas.

[†] Classification of biorefineries is still under discussion, particularly for the case of thermochemical processing of biomass. The Bioenergy Task 42 (International Energy Agency) has as its objective the classification of biorefinery systems and has proposed a classification method based on four features (i.e. platforms, products, feedstocks and processes) [45]. Although this classification method is useful, e.g. for C_5/C_6 sugars and lignin platform systems, it may not be best option in order to make a thorough classification of biorefineries using syngas as a platform [46].

The production of fuels, chemicals and services from syngas presents little or none differences if coal or natural gas were used as feedstock. However, the benefits of the use of biomass instead of such fossil fuels are well-known. Biomass has a better GHG (greenhouse gas) balance (could even be negative regarding the process), it enhances the security of the energy supply (in case biomass is produced in the same region) and it is the only renewable source for carbon based fuels and chemicals (essential for the production of for example fibers, plastics or jet fuel). For instance, the use of biomass via thermochemical processing is related to the former carbochemistry and the production of chemicals via reforming of natural gas. The fact of being close to current petrochemical facilities should be considered as an advantage, since both the technology and the know-how from the processing of fossil fuels can be adapted and integrated in BTL/G plants and thermochemical biorefineries. Of course, the use of petrochemical technologies involves that BTL/G plants and thermochemical biorefineries should be large enough to achieve the benefits of the economy of scale as in petrochemical facilities.

Contrary to current BTL/G processes, in a thermochemical biorefinery multi-production is the main objective. In a thermochemical biorefinery the existence of a platform chemical brings different options for multi-production. The platform chemical could be a product itself or converted into more products, i.e. following two (or more) different routes resulting in different products. The design of thermochemical biorefineries is of greater complexity than in the case of BTL/G processes. The chemical routes assessed in studied BTL/G processes could be used in the design of thermochemical biorefineries (combining two or more), but as they are not properly suitable for multi-production, the review of other routes (especially for the production of chemicals) is of interest. In this context, several routes were proposed for the production of chemicals and fuels from syngas in the 1980s due to the crude oil crisis, which promoted the search of an alternative feedstock (i.e. natural gas or coal) to substitute crude oil for chemical and fuel production. In some routes, syngas was converted into methanol, which is a platform chemical for the production of for example, gasoline (Methanol-To-Gasoline –MTG–) and olefins (Methanol-To-Olefins –MTO–). Biomass and carbon-based waste are also suitable as crude oil substitutes, since the processing downstream of syngas conditioning is identical. The main advantage of routes via platform chemicals for the design of new concepts of thermochemical biorefineries is their capability to be combined or slightly modified to achieve multi-product generation, as has been already demonstrated [44].

In this review, the most appealing platform chemicals suitable for the design of thermochemical biorefineries have been identified, namely: methanol, DME and ethanol. In section 2, compiled routes via platform chemicals are described and revised in detail, while the well reported MTG and MTO routes are only briefly reviewed. Implications of the use of biomass and carbon-based waste are also detailed together with one example of thermochemical biorefineries based on DME as the platform chemical.

1.1. General aspects of thermochemical processing

Selection of the thermal treatment of biomass depends on further use of the product. For BTL/G processes the thermochemical processing of biomass usually involves gasification or pyrolysis [47-50]. This review will focus only on synthesis routes via gasification.

1.1.1. Gasification, gas cleaning and conditioning

Gasification of all carbon-based feedstocks (biomass, coal, carbon-based waste) undergoes the same basic chemistry and thermodynamics [51]. The gasification process can take place at temperatures in the range of 800 °C to 1800 °C, but in the case of biomass gasification, temperatures are always below 1300 ºC due to softening and melting temperatures of the biomass ashes [51]. Currently, entrained flow bed (EF) and circulating fluidized bed (CFB) operated with oxygen and steam, and indirect circulating fluidized bed (i-CFB) operated with air are the proposed gasification technologies for syngas production from lignocellulosic biomass [13,14,20,26,39,52]. Gasification of carbon-based waste is also feasible but the variability of its chemical composition makes it technologically more difficult [51]. Raw syngas from the gasifier needs different cleaning and conditioning treatments, which depend on the further processing of syngas.

2. Routes via platform chemicals

The chemistry of these routes is always characterized by the presence of at least one chemical intermediate (platform chemical) generated from syngas. The platform chemical can be directly converted into products or converted into a new chemical intermediate. Most routes were initially proposed in the 1980s as consequence of the crude oil crisis, since they allow replacing crude oil with coal and natural gas with the production of commodities and fuels. The recovery of crude oil prices led to their abandonment; however, their use has recently been reconsidered for the processing of biomass. Figure 1 shows the routes via platform chemicals which have been reviewed. Most routes are based on the use of methanol or DME, which is easily generated from methanol (dehydration). Ethanol is also included as a platform chemical, although bioethanol is usually not produced from syngas, but directly from biomass.

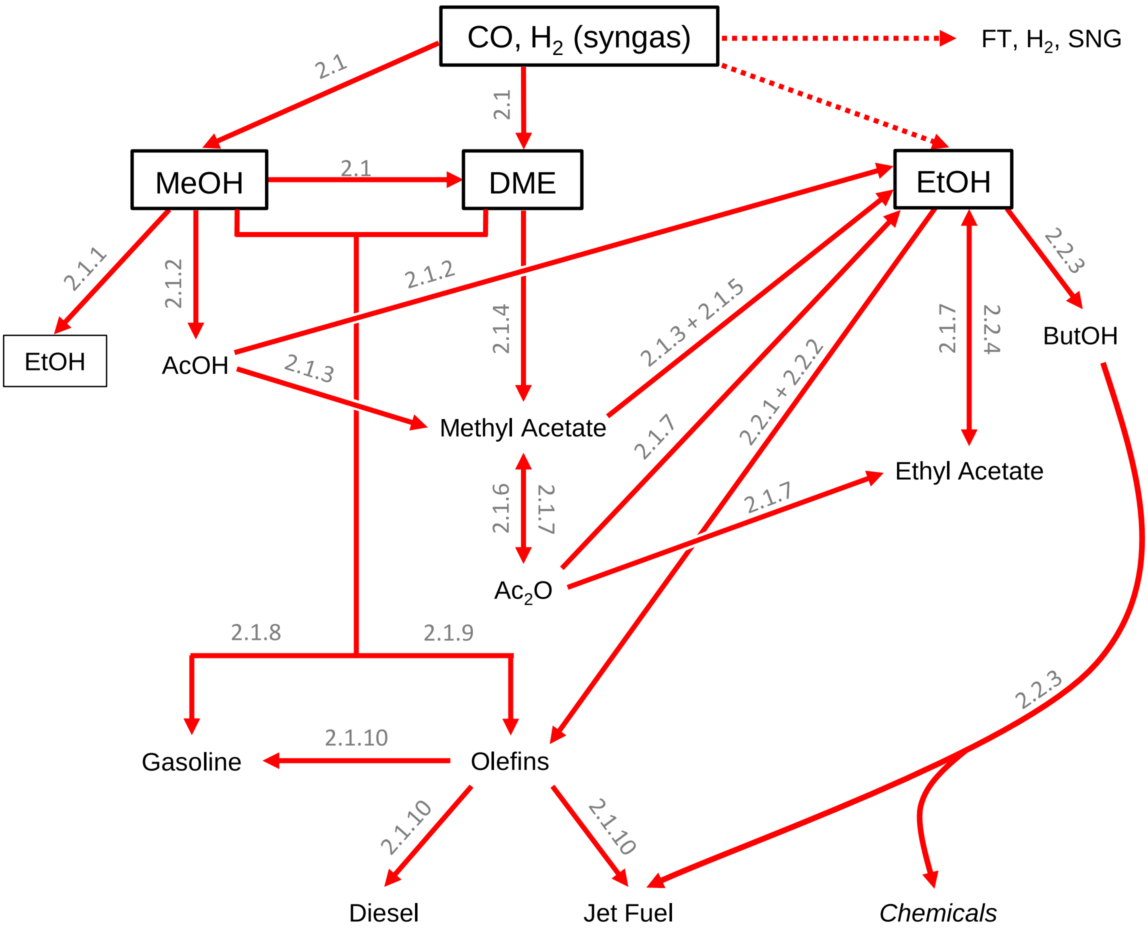

Figure 1. Thermochemical routes via platform chemicals (methanol/DME and ethanol) for the production of chemicals and fuels from syngas.

The chemical equations which are involved in routes via platform chemicals are presented below:

$CO + 2H_2 \rightarrow CH_3OH$ (1)

$CO + H_2O \rightarrow CO_2 + H_2$ (2)

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ (3)

$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ (4)

$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2$ (5)

$CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O$ (6)

$CH_3OH + 2CO + H_2 \rightarrow C_2H_5OH + CO_2$ (7)

$CH_3OH + CO \rightarrow CH_3COOH$ (8)

$CH_3COOH + 2H_2 \rightarrow C_2H_5OH + H_2O$ (9)

$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$ (10)

$CH_3COOH + C_2H_5OH \rightarrow CH_3COOCH_2CH_3 + H_2O$ (11)

$CH_3COOCH_3 + 2H_2 \rightarrow C_2H_5OH + CH_3OH$ (12)

$CH_3COOCH_2CH_3 + 2H_2 \rightarrow 2C_2H_5OH$ (13)

$2CH_3OH + CO \rightarrow CH_3COOCH_3 + H_2O$ (14)

$CH_3OCH_3 + CO \rightarrow CH_3COOCH_3$ (15)

$CH_3OCH_3 + CO + 2H_2 \rightarrow C_2H_5OH + CH_3OH$ (16)

$CH_3COOCH_3 + CO \rightarrow (CH_3CO)_2O$ (17)

$(CH_3CO)_2O + C_2H_5OH \rightarrow CH_3COOCH_2CH_3 + CH_3COOH$ (18)

$(CH_3CO)_2O + CH_3OH \rightarrow CH_3COOCH_3 + CH_3COO$ (19)

$C_2H_5OH \rightarrow C_2H_4 + H_2O$ (20)

$2C_2H_5OH \rightarrow C_4H_9OH + H_2O$ (21)

2.1. Methanol/DME as a platform chemical

The production of methanol from syngas is well documented and represents one of the most important industrial applications of syngas [25-27,53]. Methanol synthesis (Eq. (1)) can be described as a set of two exothermic reversible reactions, namely, conversion of CO via water gas shift reaction to CO_2 (Eq. (2)) and hydrogenation of CO_2 to methanol (Eq. (3)) [54]. The catalyst used for methanol synthesis is a Cu-ZnO supported on alumina (Al_2O_3), which has been improved to achieve selectivity to methanol over 99% [54]. Typical reaction conditions for methanol synthesis are 200-300 ºC and 40-100 bar [54-55]. Industrial production of methanol is carried out using different reactor configurations. The most important reactors for commercial production of methanol are: tube cool converter, radial flow steam raising converter (R-SRC), axial flow steam raising converter (A-SRC), quench converter (*Johnson Matthey Company*) [56,57]; combined synthesis converter (*Lurgi – Air Liquid Group*) [58]; methanol super converter (*Mitsubishi Heavy Industries*) [56,59]; collect-mix-distribute (CMD) reactor, boiling water reactor (*Haldor Topsoe*) [56,57]; axial radial concept (ARC) quench type reactor, horizontal steam raising reactor, pseudo isothermal reactor (*Methanol Casale*) [56,60]; Variobar converter (*Linde AG*) [55,61]; MRF-Z converter (*Toyo Engineering*) [61]; and liquid-phase methanol (LPMEOH) reactor (*Air Products and Chemicals, Inc.*) [56,62].

DME can be produced directly from syngas (Eq. (4)) or indirectly via methanol dehydration (Eq. (5)) [63,64]. Typical reaction conditions are 250-400 ºC and up to 20 bar, using a dehydration catalyst, e.g. γ-alumina or zeolites [65,66]. Direct synthesis of DME from syngas is described in [67-69]. Typical reaction conditions are close to methanol synthesis and the catalyst employed is a mixture of methanol synthesis and dehydration catalyst [70]. In the case of methanol dehydration, industrial production of DME is carried out using fixed bed reactors, whereas in the case of direct synthesis similar reactors to those used for methanol synthesis are employed.

2.1.1. Methanol homologation to ethanol

The methanol homologation, or methanol reductive carbonylation, route was the first studied route via a platform chemical (1951) to produce ethanol from syngas and remains the most investigated to date.[71] Methanol homologation was envisioned along with direct conversion of syngas to ethanol as an alternative process to produce ethanol from coal [72]. Despite the great interest in the 1980s the methanol homologation route has been nearly disregarded and neither a pilot plant nor commercial process based on this route has been constructed [4]. For a profitable application of the methanol homologation route, development of non-toxic homogeneous catalysts which could be easily (and economically) recovered, or heterogeneous/supported catalysts achieving yields to ethanol similar to those in the case of homogeneous catalysts, are needed.

The methanol homologation route comprises two consecutive steps to make ethanol from syngas: methanol synthesis (Eq. (1)) and methanol homologation (Eq. (6) or Eq. (7)). In a possible process based on this route, syngas would be first converted in a methanol synthesis reactor and the outlet stream would be directly fed to the homologation reactor where unconverted syngas and previously generated methanol react at 150-200 ºC and high pressures (100-300 bar) producing ethanol, and to a lesser extent, oxygenates and hydrocarbons.

The methanol homologation step can be carried out via different kinds of homogeneous catalyst. The first study of methanol homologation was presented by Wender et al. using a Co-based homogeneous catalyst in a batch reactor [71]. Depending on the H_2/CO molar ratio in the homologation reactor feed, the homologation can occur by Eq. (6) or Eq. (7), resulting in the generation of either water or CO_2 as a by-product. Table 1 shows the common chemical states for the studied homologation catalysts along with the main promoters for the reaction. A detailed description of the kinetics and reaction mechanism of the homologation reaction is presented elsewhere [73-77]. The main active complex in the homologation reaction can be described by the formula $[M(CO)_n]^d$, where M represents the active component, n is the coordination factor (frequently: 3, 4, 12) and d is always negative (often -1). This complex allows itself the CO insertion in the methanol molecule. However, promoters and additives are required in order to increase the rate of reaction and selectivity, and avoid complex irreversible degradation [78]. Promoters can be present in different chemical species, e.g. CH_3I, phosphine [79,80]. Additives, mainly oxygenates compounds, affect product distribution since most are products of the secondary reactions during homologation [81-85]. These additives shift secondary reactions, which are in equilibrium, at operating conditions of methanol homologation. Attempts to use heterogeneous or supported catalysts are reported in the literature but the results obtained are still unsatisfactory [86,87].

Table 1. Chemical state for the catalyst used in the methanol homologation route.

		chemical state									***Ref.***
		Acetate	Carbonate	Carbonyl	Formate	Oxide	Carboxylate	Elemental	Chloride	Organic	
active component	Co-Rh	✓	✓	✓	✓	✓	✓	✓	✗	✗	[4 71,88,89]
	Mn	✓	✓	✗	✗	✓	✗	✓	✓	✗	[72,90]
	Fe-Rh-Mn	✗	✗	✓	✗	✗	✗	✗	✗	✗	[91–93]
promoter	I	✗	✗	✗	✗	✗	✗	✓	✗	✓	[94]
	P	✗	✗	✗	✗	✓	✗	✓	✗	✓	[85]
	Ru	✓	✗	✓	✗	✓	✗	✗	✓	✗	[94–96]

Despite the great number of patents and publications on the methanol homologation route, neither a commercial process, nor even an industrial program has been developed. The only active project, at laboratory scale, is called the *Dry Ethanol Process*, carried out by the Argonne National Laboratory [93-97]. This process follows Eq. (7), so no water is generated, and uses a Fe-Mn-based homogeneous catalyst with n-methylpiperidine as the promoter. The main advantage of this route is the absence of water in products, which makes the recovery of ethanol easier [93].

There is a lack of knowledge on the deactivation of the methanol homologation catalyst. According to Ishogai, it would be possible to use syngas with low contents of methane, ethylene and CO_2 without a significant negative impact on the catalyst [85]. Due to the scarcity of information, the experience gained from the most similar process, acetic acid synthesis (Monsanto Process), could be helpful [54,78].

The research on methanol homologation following Eq. (6) is limited at laboratory scale, but there are some patents describing preliminary conceptual designs [81,88]. In a similar way to LPMEOH synthesis, the homogeneous catalyst requires the presence of an inert solvent to carry out the reaction [81]. The solvent, e.g. the same used in LPMEOH, has to ensure liquid-liquid equilibrium (water-products/solvent-catalyst-syngas) [83]. Hence, the homologation of methanol should be carried out for example, in a batch reactor, a continuous stirred tank reactor (CSTR), a bubbling column with internal recycle, or another kind of reactor available for homogeneous catalysts. Table 2 shows a collection of reaction data for methanol homologation following Eq. (6). Although general references claim that methanol homologation needs pressures of about 300 bar, which was only true in the first stage of development of the homologation catalyst [98]. The use of promoters allowed a reduction of operating pressure, which is limited by the condition of retaining methanol as liquid in the reactor (usually limited to a total pressure of 50 bar). Detailed information on product selectivity for a catalyst with Ru can be found in Jenner [99]. Through the use of additives, ethanol selectivity is improved up to 91-93% [89].

Table 2. Reaction conditions, product distribution and main additives for homologation catalysts.

Catalyst	***reaction conditions*** [a]						**product yield (%)**								**additives** [b]
	T (ºC)	P (bar)	Residence time (min)	H_2/CO molar ratio	X_{CO}	$X_{Methanol}$	Ethanol	Propanol	Ethyl acetate	Oxygenates [c]	CO_2	CH_4	Others	Water	[81,84]
$[Co(CO)_4]_2$ [71]	180-185	205	480	1	N/A	76.4%	38.8	4.7	6.3	12.0	N/A	8.5	6.1	90.8	acetone n-propanol n-butanol methyl acetate benzoic acid
Co-I catalyst [88]	190	100	300	2	N/A	70%	52.71	11.55[d]	3.71	2.03[e]	N/A	0	0	N/A	
Rh/(Ru-I-P) [100]	140	83	180	3	N/A	NA	89[f]	NA	NA	NA	N/A	N/A	N/A	N/A	
$Co(OAc)_2·4·H_2O$ [81]	185	200	120	2	N/A	35.1%	25.5	NA	NA	NA	N/A	N/A	N/A	N/A	
$Co(OAc)_2·4·H_2O$-I-P [83]	205	200	120	1	N/A	47.0%	32.8	NA	NA	~8	N/A	N/A	~6	N/A	

[a] All collected data refers to batch reactors.
[b] Refers to all catalysts.
[c] Other oxygenates.
[d] Propanol, propanal and methyl acetate.
[e] Acetic acid.
[f] Selectivity to ethanol and acetic acid.
N/A = not available.

Table 3. Reaction conditions for the *Dry Ethanol Process*.

Catalyst	***reaction conditions*** [a]						**product yield (%)**							
	T (ºC)	P (bar)	Residence time (min)	H_2/CO molar ratio	X_{CO}	$X_{Methanol}$	Ethanol	Propanol	Ethyl acetate	Oxygenates [b]	CO_2	CH_4	Others	Water
Fe-Rh-Mn [93-97]	180-220	300	360	1/3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

[a] All collected data refers to batch reactors.
[b] Other oxygenates.
N/A = not available.

2.1.2. Methanol to ethanol via acetic acid hydrogenation

The acetic hydrogenation route comprises a set of common steps: methanol synthesis (Eq. (1)), acetic acid synthesis (Eq. (8)) and acetic acid hydrogenation (Eq. (9)). As shown in Figure 2, syngas is used for methanol synthesis, as commented in section 2.1., and also to provide CO for the synthesis of acetic acid. Produced methanol is carbonylated using a homogeneous catalyst. Acetic acid is then directly hydrogenated to ethanol and water. Regarding the conditions of the acetic acid hydrogenation, i.e. considered catalyst and reaction conditions, more steps could be needed for subproduct conversion by recycling or chemical conversion in additional reactors [101].

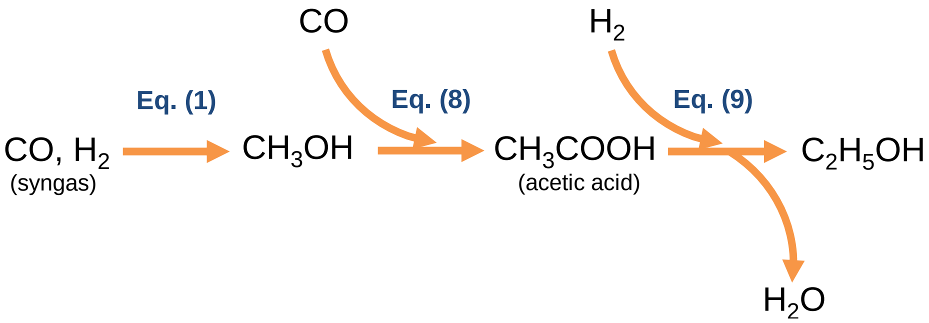

Figure 2. Chemical scheme for the acetic acid hydrogenation to ethanol.

The acetic acid hydrogenation route was developed in the early 1980s [4]. This route is based on the hydrogenation of acetic acid to yield ethanol, and to a lesser extent, acetates using heterogeneous catalysts. The employment of a heterogeneous catalyst is the main advantage of this route compared with the methanol homologation route. As in the case of methanol homologation, the end of the crude oil crisis was the main reason for its withdrawal, but in the case of the acetic acid hydrogenation route, the corrosiveness of the reaction mixture (with a detrimental effect on the life of hydrogenation catalyst) was also determinant [101-103].

The synthesis of acetic acid is one of the most important examples of industrial processes using homogeneous catalysts. When the hydrogenation of the acetic acid route was in the first stage of development, conventional synthesis of acetic acid was mainly conducted via the Monsanto process operating at 150-200 ºC and 30-60 bar with very high selectivity to acetic acid [104]. The Monsanto process uses a Rh-based homogeneous catalyst, which is converted in-situ into an active Rh-carbonyl catalyst as described in 2.1.1. for methanol homologation [104]. Currently, BP’s Cativa process has emerged as the best available technology for acetic acid production [105]. The Cativa process is similar to Monsanto’s except for the catalyst. In the Cativa process an Ir-based catalyst is used, featuring a higher catalyst lifetime and better stability and recovery [105,106].

The hydrogenation of acetic acid is carried out at liquid phase (and high H_2 pressure) using a conventional catalyst for organic compound hydrogenation [107,108]. Typical reaction conditions for the ENSOL process are 230-270 ºC and 40-120 bar [108]. A detailed description of kinetics and reaction mechanisms along with catalyst behavior can be found elsewhere [103,109-111]. Catalysts considered in the literature for acetic acid hydrogenation to ethanol are Co, Cu, Fe-based dispersed on silica support [112], supported Pt-based [103,109,110] and Pd-based catalyst [111,113]. These studies differ from the ENSOL process in operating conditions. Whereas the BASF process achieves near complete conversion of acetic acid at moderately high pressures (40-120 bar) [108], the other studies always operated at near atmospheric pressure and achieve very low per pass conversion of acetic acid (around 5%) with high lights formation [107,112]. According to the reaction mechanism, acetaldehyde is the main intermediate of the reaction and sometimes the reaction could not proceed further depending on catalyst and operating conditions (partial pressure of H_2) [111]. Therefore, acetic acid conversion to acetaldehyde is the subject of more studies in the literature than to ethanol. The reaction is quite selective to ethanol, ethyl acetate and n-butanol being the only by-products in the aqueous phase, and with low gas formation (CO and methane) [108]. Both liquid by-products can be partially converted into ethanol by recycling them into the reactor [108]. The reaction mixture (aqueous phase) is highly corrosive, which leads to rapid catalyst degradation, and becomes the main limitation for the reaction. Although reaction in the vapor phase could avoid catalyst degradation by reducing the corrosiveness of the reaction mixture, extremely high partial pressures of H_2 (of at least 270 bar) would be needed [108]. Recent efforts to produce new catalysts for the hydrogenation of acetic acid have been conducted by Range Fuels Inc. and Celanese International Corp [114,115]. Celanese has developed a Pt-Sn catalyst (see Table 4) that allows higher productivity for acid acetic hydrogenation to an ethanol/ethyl acetate mixture with remarkably high space velocity and global selectivity (to both ethanol and ethyl acetate) [115]. Other recent improvements in hydrogenation catalysts, i.e. nano Pd-based catalyst, have been carried out by BASF [116].

Table 4. Reaction conditions and product distribution for acetic acid hydrogenation catalysts.

catalyst	***reaction condition*** [a]					**product yield (%)**					
	T (ºC)	P (bar)	GSHV (h^{-1})	H_2/acetic acid	Conversion	Ethanol	Ethyl acetate	Oxygenates [b]	CO_2	CH_4	Others
Co-Cu-Mn-Mo [108]	230-270	40-120	N/A	2.1	100	97	N/A	N/A	N/A	0	N/A
Pt-Sn [115]	250	14-22	2500	10-4	22-43	15-40	3-7	0	0	0	N/A
Co-Mo-S-K [114]	325	100	6372[c]	N/A	100/72.2%[d]	NA	N/A	N/A	N/A	N/A	N/A

[a] Referred to all catalysts.

[b] Other oxygenates.

[c] Defined as $L/(kg_{cat}\cdot h)$.

[d] Conversion of acetic acid.

N/A= not available

The ENSOL process was developed by a joint-venture between Humphreys & Glasgow Ltd., Monsanto and BASF based on the acetic acid hydrogenation route, but neither a pilot plant nor further research has been done [107]. According to the original scheme of the process, methanol is produced either on-site or off-site using natural gas as feedstock. If methanol is produced on-site, it can be used as raw methanol without enhanced purity [107]. Acetic acid is produced from CO and methanol, and further converted into ethanol by hydrogenation (see Figure 2). As water is produced in the hydrogenation of acetic acid, a dewatering section is also required in the process [107]. A combination of cryogenic distillation and pressure swing adsorption (PSA) was considered the technical solution to achieve the required purity of CO and H_2 streams [107]. The requirement of high purity CO and H_2 streams represents a disadvantage of this route, since it is intensive in both energy and economy. However, the main limitation for further development of this route lies in the degradation of the catalyst for the acetic acid hydrogenation.

On the basis of reaction data from the Pacific Northwest National Laboratory, which made a technoeconomic assessment of this route, the calculated ethanol minimum selling process was higher than current market price [108,117]. In this assessment, CO and H_2 for both acetic acid production and hydrogenation were assumed as raw materials, i.e. they were not produced from biomass. A new process configuration has been recently described by Jetvic et al. [118].

2.1.3. Methanol to ethanol via acetic acid esterification

The acetic acid esterification route comprises a set of different processes in which one mole of acetic acid is esterified with one of alcohol to give one mole of the corresponding ester. The produced ester is easily hydrogenated (hydrogenolysis) to alcohols, yielding two moles of alcohol per mole of ester. One mole of alcohol is used for the esterification of acetic acid, whereas the other would be the product. To our knowledge, only two alcohols have been studied, i.e. methanol and ethanol. Chemical schemes for both cases are shown in Figure 3 and Figure 4. Although this route was developed in the early 1980s only recently have some processes become commercial, such as that by Enerkem Inc. which uses MSW as feedstock [101,119,120].

In this route, acetic acid can be produced as described in 2.1.2., or via “acid carbonylation” (combination of Eq. (8) and Eq. (14)). The first case is applicable for both methanol and ethanol, whereas the second makes sense only if the considered alcohol for the esterification is methanol. The methanol acid carbonylation is close to common acetic acid synthesis but, in this case, it is carried out in acid conditions leading to *in situ* esterification of part of the generated acetic acid with methanol [121-127]. For acid carbonylation, typical molar selectivity to both acetic acid and methyl acetate is up to 80%, with a 3:1 molar distribution of acetic acid and methyl acetate, respectively [121,126,127]. Reaction conditions for the acid carbonylation of methanol are presented in Table 5. The *in situ* esterification reduces the size of the acetic acid esterification section, since a fraction of methyl acetate is produced in the carbonylation reactor. More information about methanol carbonylation over heterogeneous catalysts can be found elsewhere [128-133].

The esterification of methanol and acetic acid is an equilibrium-limited reaction, like most esterification reactions, which can be conducted in regular fixed-bed reactors, but it is normally conducted by reactive distillation [135]. The reactive distillation of acetic acid and methyl acetate is currently the best available technology (BAT) for the production of methyl acetate [136]. The reaction system was developed by the Eastman Kodak Company and it uses an acid catalyst, e.g. sulfuric acid or a sulfonic acid ion exchange resin, for the esterification [137,138].

Esterification of ethanol and acetic acid is also an equilibrium-limited reaction, but in this case, a ternary azeotrope is present [101,139]. Industrial production of ethyl acetate can be conducted in batch or CSTR reactors along with several distillation columns [140]. The same considerations as in the esterification with methanol are applicable for the catalyst [139]. There are also studies on vapor-phase esterification, including in a supercritical CO_2 atmosphere, but they are not commercially viable [139,141,142].

Table 5. Reaction conditions and product distribution for methanol acid carbonylation catalysts.

Catalyst	***reaction condition***					**product yield (%)**	
	T (ºC)	P (bar)	GSHV (h^{-1})	CO/methanol molar ratio	Conversion	Methyl acetate	Acetic acid
Rh-I-triphenylphosphine [122]	175	40	1	N/A	64.0% Methanol	41,6	22.4
Rh-Ir[c] [134]	255	10	2500	2	99.8% Methanol	80.1	18.3
Rh-Ir-I[c] [126,127]	150-200	15-50	2000-10000	1-0.2	100% CO	50-75	25-50

[a] Referred to all catalysts.

[b] Other oxygenates.

[c] Supported catalyst (on activated carbon).

N/A= not available.

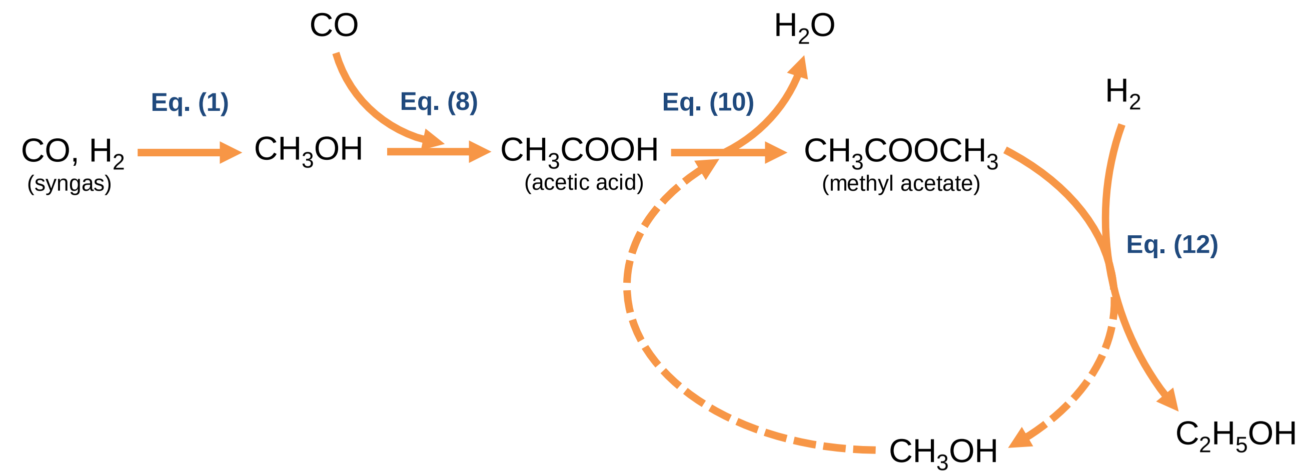

Figure 3. Chemical scheme for the acetic acid esterification with methanol.

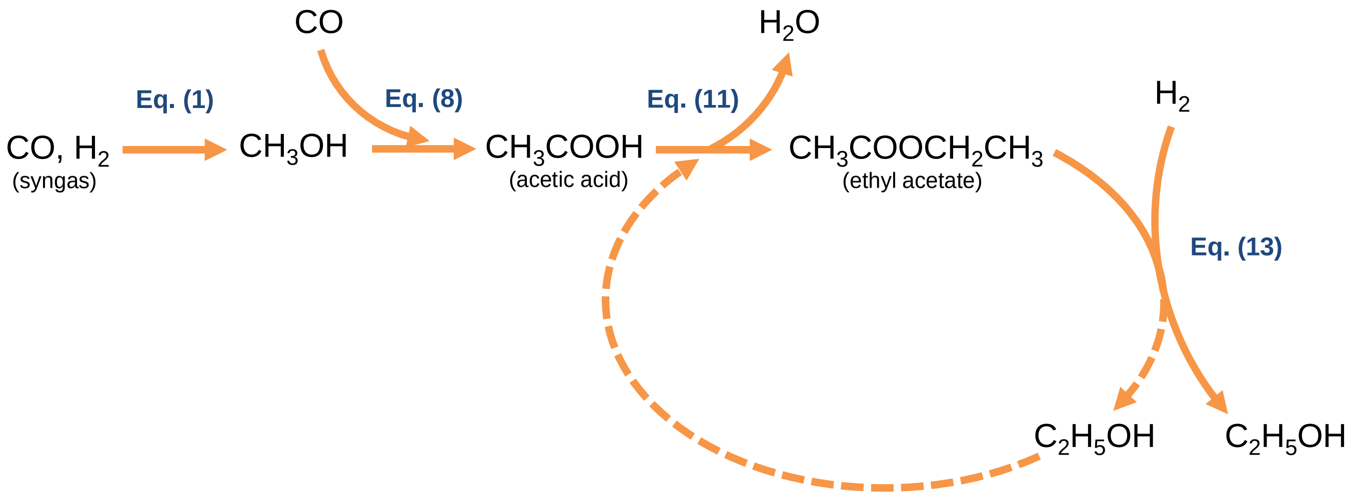

Figure 4. Chemical scheme for the acetic acid esterification with ethanol.

Hydrogenation (hydrogenolysis) of methyl or ethyl acetate is carried out with heterogeneous catalysts in fixed-bed reactors. Various catalysts have been used for both reactions but at reaction conditions. For common Cu-Cr (Adkins) catalysts reaction conditions are severe, i.e. 250–350 °C and a partial pressure of H_2 of 100-300 bar [122,143]. Other catalysts used for acetate hydrogenation are Cu-Fe [144], Re-based [145], Pd-ZnO [146], hydrotalcites [143], Ni-based [147] and Rh-based catalysts [148]. Reaction conditions for these catalysts are close to those from the Cu-Cr catalyst, but with lower H_2 pressures (up to 60 bar) [143]. Ethanol selectivity ranges from 60 to 95%, the main by-products being higher acetates (produced by homologation of the original acetate) and acetaldehyde. However, in these previous studies, acetate hydrogenation (hydrogenolysis) is carried out in the absence of CO. Recent publications based on a Cu-ZnO catalyst claim that the hydrogenation of acetates (methyl and ethyl acetates) can be carried out in the presence of CO with a H_2 to CO molar ratio of 1, at lower partial pressures of H_2 (<15 bar) and with similar or higher selectivity to corresponding alcohols [149-151].

The Halcon SD Group proposed a process based on the acetic acid esterification route for the production of ethanol using methanol and natural gas as feedstock [101]. In this process, methanol is carbonylated to produce acetic acid using a proprietary technology similar to Monsanto’s process. Esterification of acetic acid is carried out with methanol recycled from the hydrogenation section using proprietary technology (Eastman Kodak). Produced methyl acetate is hydrogenated to yield an equimolar mixture of methanol and ethanol. CO and H_2 for the process are produced by reforming natural gas [101]. BASF AG proposed another alternative based on this route which used acid carbonylation (see Table 5) [122]. In this process, methanol is carbonylated to yield a mixture of methyl acetate, acetic acid, DME, and to a lesser extent, ethanol and propionic acid [122]. Produced methyl acetate is then hydrogenated, as commented before. In this process, acetic acid from the acid carbonylation is recycled to the carbonylation reactor for total conversion to methyl acetate. There are other process alternatives such as that by the Korea Institute of Science and Technology, which proposed a supported catalyst for the acid carbonylation of methanol with no recycling of acetic acid [134].

Recently, Enerkem Inc. has proposed the modification of previous BASF and Korea Institute of Science and Technology processes by adding a stage for acetic acid esterification in order to achieve complete conversion to methyl acetate [126]. In this process, methanol is carbonylated to a mixture of methyl acetate and acetic acid in the vapor phase using a fixed bed reactor packed with a rhodium-based catalyst [127]. Acetic acid is further esterified with methanol by reactive distillation yielding methyl acetate. Methanol from the hydrogenation of methyl acetated is recycled to esterification section. If ethanol is used instead of methanol for the esterification, only ethanol would be produced (hydrogenation of ethyl acetate, Eq. (13)) and no distillation of the methanol/ethanol mixture would be required. However, the use of ethanol does not result in the reduction of costs, due to the greater complexity of the acetic acid esterification [101].

Enerkem has announced that they expect to produce competitive bioethanol in the short term with their process [120].

2.1.4. Methanol/DME to methyl acetate via DME carbonylation

The DME carbonylation route relates the production of methyl acetate through DME by using only heterogeneous catalysts. This route is based on the capability of some catalysts, e.g. zeolites, to synthetize methyl acetate from CO and DME. The carbonylation of DME to yield methyl acetate is a new and active field of research [152]. Although this route can be integrated with acetic anhydride production (see 2.1.6.), it is preferable to discuss each one separately, since they are focused on a different product. Methyl acetate is currently available as a subproduct in the commercial production of acetic acid or produced by reactive distillation from acetic acid and methanol [153]. The uses of methyl acetate are as a solvent (substitute for acetone), and for the production of acetic anhydride [154,155].

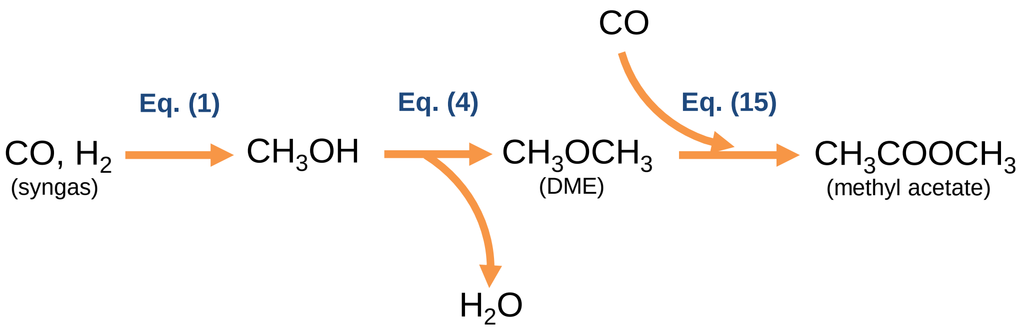

Figure 5. Chemical scheme for DME carbonylation.

The DME carbonylation route comprises the combination of DME synthesis and DME carbonylation (Eq. (15)), as shown in Figure 5. Syngas is used for DME synthesis (see 2.1.) and to provide CO for the carbonylation of DME, which (depending on the syngas composition and plant configuration) normally leads to a net production of H_2.

The carbonylation of DME occurs in the presence of some kinds of zeolites, e.g. mordenites, ferrierites and ZSM-35, at reaction conditions of up to 100 bar and 150-200 ºC [131,156,157]. The carbonylation reaction is said to be conducted with a stable rate and without significant catalyst deactivation [131,156]. Presence of water in the reaction mixture decreases methyl acetate formation and slightly increases that of methanol. This is because of the competition of water for the active sites of the zeolite [131,152]. However, this effect is reversible and does not deactivate the catalyst [131]. Methyl acetate synthesis rates are proportional to CO pressure and independent of DME [131]. DME carbonylation is primarily conducted in 8-MR channels, in the case of mordenites, or in 10-MR channels, in the case of ZSM-35 [156,157]. There is a possible deactivation due to coke formation on the catalyst [132,157]. Details for the kinetics of the DME carbonylation are given elsewhere [133,152,156,158]. The DME carbonylation route has been technoeconomically assessed along with the DME hydrocarbonylation route (see

2.1.5.) [44]. Results showed that methyl acetate can be produced economically from lignocellulosic biomass.

2.1.5. Methanol/DME to ethanol via DME hydrocarbonylation

The DME hydrocarbonylation route is the most recent attempt to find a feasible technoeconomic route to produce ethanol from lignocellulosic biomass [44,52,149-151,159]. The DME hydrocarbonylation route is an extension of the DME carbonylation route (2.1.4.), where a hydrogenation step is added leading to ethanol production. In this route, produced methyl acetate is hydrogenated (see 2.1.3.) to yield methanol, which is recycled to complete conversion, and ethanol. For ethanol production, the DME hydrocarbonylation route outweighs the above described processes focused on ethanol production (with acetic acid as intermediate), since the number of process steps is lower and only heterogeneous catalysts are employed.

The DME hydrocarbonylation route (Figure 6) comprises the following steps (some alternatives are possible): DME synthesis (see 2.1.), DME hydrocarbonylation (Eq. (16)) and methanol dehydration (Eq. (4)). The hydrocarbonylation of DME has been studied in a dual catalytic bed reactor, where catalysts for carbonylation of DME and hydrogenation of methyl acetate were placed in series [149-151,159]. Results of these studies show that the hydrocarbonylation can be effectively conducted at 220 ºC and 15 bar using the combination of a first catalytic bed of H-Mordenite and a second catalytic bed of Cu-ZnO [149-151].

The DME hydrocarbonylation route has been technoeconomically assessed [44,52]. The results showed that the DME hydrocarbonylation route is cost-competitive for ethanol production from lignocellulosic biomass, due to the mild reaction conditions and high global selectivity to ethanol.

2.1.6. Methanol/DME to acetic anhydride via methyl acetate carbonylation

The methyl acetate carbonylation route was developed in the 1980s in an attempt to overcome the ketene process in the synthesis of acetic anhydride [136,160]. Acetic anhydride is one of the most important organic intermediates in the industry and it is used for the production of cellulose acetate and as a precursor of vinyl acetate monomer [161]. In the methyl acetate carbonylation route, acetic anhydride is produced through acetic acid (Eq. (8,10)) or DME (Eq. (4,15)), which leads to the two alternatives shown in Figure 7. Acetic anhydride production through acetic acid represents, along with the ketene process, the main commercial means of acetic anhydride production [136,161].

The carbonylation of methyl acetate is a process derived from methanol carbonylation (see 2.1.2.), using Rh-based homogeneous catalysts. In methyl acetate carbonylation, H_2 has to be present as a reduction agent for the catalyst, and also to avoid acetic anhydride hydrolysis.

Other differences between methyl acetate and methanol carbonylation relate to the choice of promoters (LiI) and the reaction mechanism, as described by Zoeller [136,162].

The Eastman Kodak Company, in collaboration with the Halcon SD Group, proposed the first commercial process using methyl acetate carbonylation. The process aimed to use coal as feedstock and the final product would be cellulose acetate [136,160]. In this process, methyl acetate reacts with CO to yield acetic anhydride which is converted in the plant into cellulose acetate. Reaction of acetic anhydride and cellulose leads to the production of acetic acid as a by-product, which is used for the esterification with methanol [136].

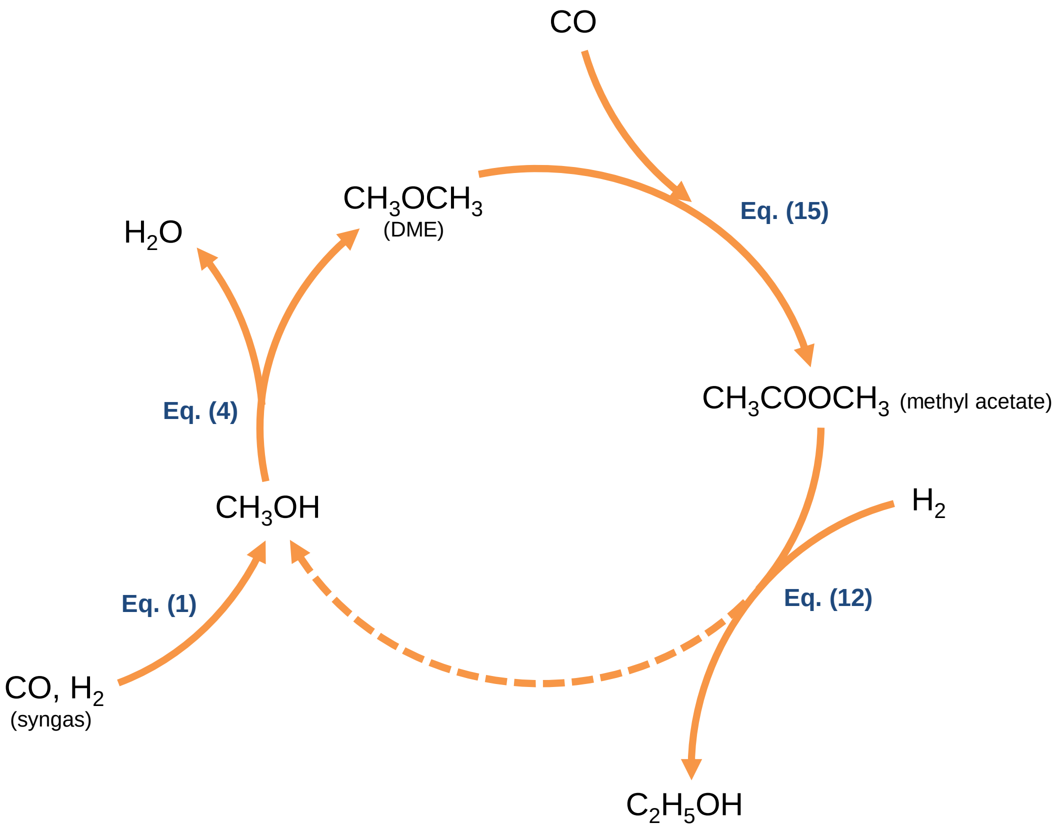

Figure 6. Chemical scheme for the DME hydrocarbonylation route. Adapted from Haro et al. [44]. The dashed line means recycling.

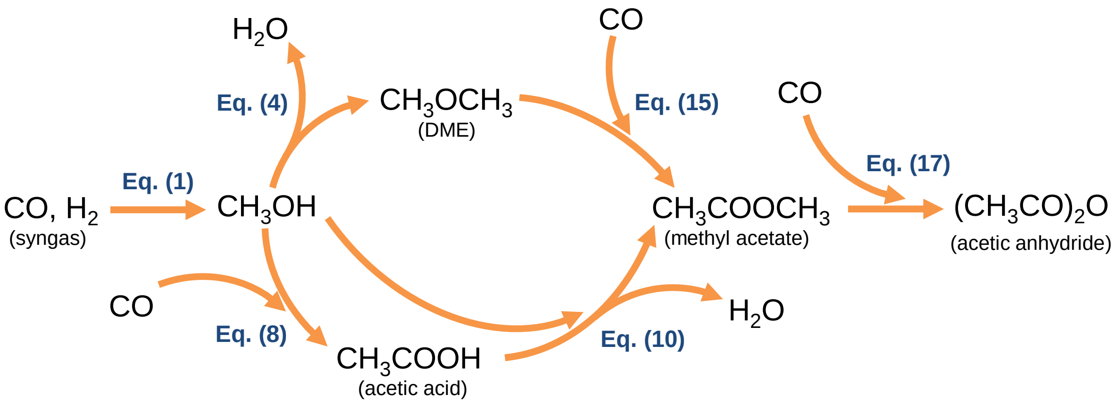

Figure 7. Chemical scheme for methyl acetate carbonylation through DME.

2.1.7. Methanol to ethanol via acetic acid esterification

The acetic anhydride esterification route was proposed by the Halcon SD Group in the 1980s [101,160,163]. This route relates to the capability of acetic anhydride to yield acetates via esterification with alcohols. Several process configurations are applicable to this route, but only two are appealing. In both configurations the main product is ethanol. However, neither has been commercialized or further investigated.

In the first alternative, methanol reacts with acetic acid (see 2.1.3.) to form methyl acetate, which is then converted into acetic anhydride by carbonylation with CO (Eq. (17), see 2.1.6.) [163]. The acetic anhydride is esterified with ethanol (Eq. (18)) to yield ethyl acetate and acetic acid. Acetic acid is recycled to the first esterification (Eq. (10)), whereas ethyl acetate is hydrogenated to ethanol (Eq. (13)). A fraction of generated ethanol is used for the esterification with acetic anhydride (see 2.1.3). Figure 8 shows the chemical scheme in the case of acetic acid esterification with ethanol.

In the second alternative, an equimolar mixture of methanol and ethanol react with acetic anhydride to yield a mixture of methyl and ethyl acetate, (Eq. (19) and (18)) [101]. Methyl acetate is recycled for acetic anhydride production (Eq. (17)) and ethyl acetate hydrogenated (Eq. (13)) to yield ethanol as a product.

2.1.8. Methanol/DME to gasoline

The methanol-to-gasoline (MTG) route was developed in the 1980s in response to the crude oil crisis. The considered feedstock was natural gas, as a substitute to crude oil, which made the process especially attractive for isolated locations with access to natural gas [164,165]. The first commercial plant based on the MTG route was constructed in New Zealand (1985) using fixed-bed technology [166]. Other facilities were constructed, but most of them were shut down when crude oil prices made the process unprofitable [164]. DME can also be used (and is sometimes preferred for the thermal integration of the reactor) as the chemical intermediate for conversion to gasoline [167]. At present, there is new interest on this route, not focused only on natural gas as the feedstock but also on coal and biomass. Exxon Mobile and Haldor Topsoe are the most important licensors of this technology.

Kinetics for methanol/DME to gasoline conversion is described elsewhere (focused on methanol conversion) [164,168,169]. Methanol/DME to gasoline conversion is a complex reaction pattern of methylation, oligomerization, hydrocarbon formation and cracking using zeolites as catalysts [168,169]. Further discussion on process technologies and other aspects such as catalyst deactivation can be found in Olsbye et al. [166]. The conversion of methanol/DME into gasoline results in light gases, hydrocarbons in the light and heavy gasoline range, and water. The most problematic compound of the heavy gasoline fraction is durene (1,2,4,5-tetramethyl-benzene) which needs to be further processed in order to meet current gasoline specifications [170]. The upgraded heavy gasoline is blended with the light gasoline fraction to give commercial grade gasoline.

Both fixed-bed and fluidized bed technologies have been proven for the MTG route in commercial plants. Details of process design and plant economics are given elsewhere [164,165,171]. Technoeconomic assessments on gasoline production from lignocellulosic biomass have been recently published [21,170,172,173].

2.1.9. Methanol/DME to olefins

The methanol/DME to olefins (ethylene and propylene) route was developed simultaneously with the methanol/DME to gasoline route and both routes have important similarities [164,172]. Regarding conversion section, UOP has developed the so-called methanol-to-olefins (MTO) process using a fluidized catalytic reactor [164,166,168]. This design is the best available technology for methanol conversion to olefins [164].

Details for the kinetics and reaction conditions for the methanol/DME conversion into olefins are presented elsewhere [164,166-169]. In general, catalysts (zeolites) for the production of olefins are characterized by smaller pore sizes compared to the production of gasoline [169]. Lower partial pressures of DME and higher reaction temperatures lead to a shift in the product distribution to lighter hydrocarbons [167]. The main products are ethylene and propylene, making up about 84% on mass basis of total hydrocarbons produced [164,174].

This route has been recently assessed [172]. Results showed that olefins could be produced efficiently from lignocellulosic biomass but at higher costs than current production, mainly due to the feedstock price.

2.1.10. Methanol/DME to fuels (gasoline, diesel and jet fuel)

In this route, olefins are converted into hydrocarbons in the range of gasoline, diesel and jet fuel. The conversion of olefins can be conducted in a fixed-bed reactor at variable reaction conditions which leads to different productions of each fraction. A description of such a process is given by Avidan and was developed by Mobil [164,175]. Despite the greater complexity of this route, the gasoline fraction is usually better quality, as the durene content is lower compared to gasoline produced via the MTG route (2.1.8.) [164,169,175]. However, there is a lack of public information on specific reaction conditions and process configuration.

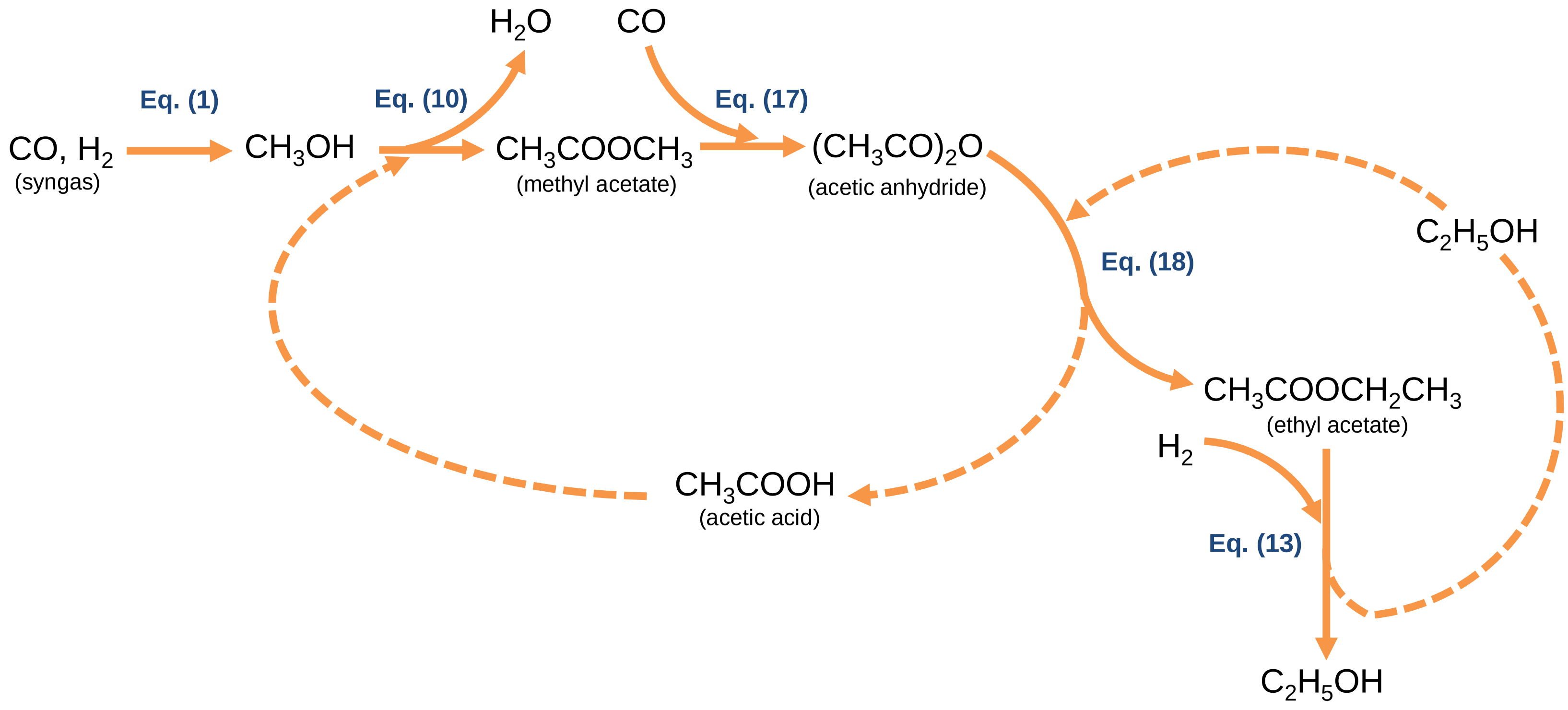

Figure 8. Chemical scheme for the acetic anhydride esterification route (with ethanol). Dashed lines mean recycling.

2.2. Ethanol as a platform chemical

The following routes relate to the use of ethanol as a platform chemical. Obviously, these routes are independent of the origin of ethanol, which could come from lignocellulosic biomass (2nd generation processes), e.g. from sugar cane, corn or sugar beet (1st generation processes), or even from a fossil feedstock, as commented in 2.1.1., 2.1.2., 2.1.3. and 2.1.5. Hence, the discussion will include the processing of all kinds of ethanol regardless of their provenance.

2.2.1. Ethanol dehydration to ethylene

The ethanol dehydration route relates to the production of ethylene using ethanol. There is growing interest in this route, since the apparent relatively low-cost of bioethanol makes it attractive for chemical synthesis [176]. Ethylene production from ethanol represents one of the most feasible options at present from both a technical and economic point of view [177]. The dehydration of ethanol is an established technology which is commercially available [176,178]. Some industrial projects are currently being carried out [179].

The dehydration of ethanol (Eq. (20), Figure 9) is conducted at 180-400 ºC and atmospheric pressure achieving selectivities of over 95% to ethylene [176,179-183]. As in the case of methanol dehydration (see 2.1.), zeolites are the preferred catalyst for ethanol dehydration, but a carbon-based catalyst has also been studied [180,184]. Main by-products depend on the employed catalyst, but the most cited are ethane, propylene, butylene and diethyl-ether [178,180,181]. Presence of water in the reaction mixture has an important effect on selectivity to by-products and on ethanol conversion [180,181]. Water prevents catalyst deactivation due to coke formation [180]. Details on the kinetic and process conditions can be found elsewhere [180-183,185].

The BETE (bioethanol-to-ethylene) process was studied in the 1980s as an attempt to use raw ethanol from 1st generation processes as feedstock [185]. However, there is no new information about this process. Currently, there are several projects in Brazil, due to the availability of low-cost ethanol [176,186]. A technoeconomic assessment for ethylene production using bioethanol as feedstock has been recently carried out [187].

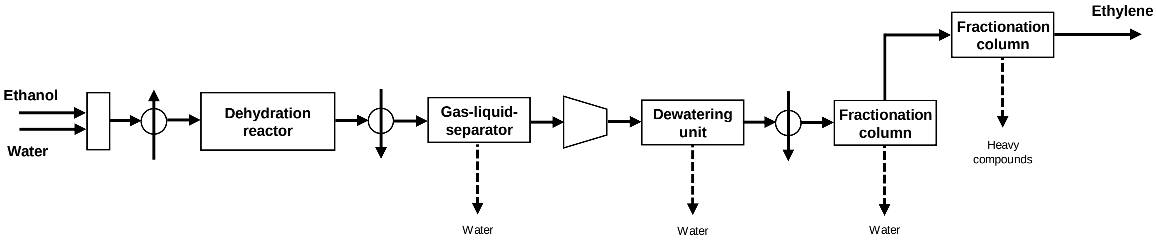

Figure 9. Conceptual diagram for the ethanol dehydration route.

2.2.2. Ethanol to propylene

Propylene can be produced from ethanol [188]. In this route, the ethanol feedstock is dehydrated to ethylene (see 2.2.1.) and then a portion of ethylene is dimerized to produce normal butene. The butenes are then reacted with the remaining ethylene via the metathesis reaction to produce propylene [188]. The chemistry of olefins metathesis is described elsewhere [189,190].

2.2.3. Ethanol to butanol

Recently, some companies have focused their efforts on the production of renewable butanol from ethanol, because of the enhanced properties of butanol as a gasoline substitute and as a chemical precursor [191]. The conversion of ethanol to butanol (Eq. (21)) is called catalytic condensation, dimerization or reductive dehydration. Some catalysts are active for the reaction: MgO [192], hydroxyapatites [193,194], Cu-Mg-Al mixed oxides [195] and hydrotalcites [196,197]. Depending on the selected catalyst, the reaction is conducted at temperatures ranging from 250 to 450 ºC and atmospheric pressures [192-195,197]. Details of ethanol conversion to butanol are given elsewhere [192-198]. Technological development of this route is still limited and public technoeconomic assessments on the routes are scarce [199].

Butanol can be further processed for the production of renewable jet fuel and chemicals but further research is still needed to optimize process conditions and quality of the fuel [200-202].

2.2.4. Ethanol dehydrogenation to ethyl acetate

Ethanol can be dehydrogenated to yield ethyl acetate, i.e. the reverse reaction to Eq. 13 (see 2.1.7.). The chemistry basis of ethanol dehydrogenation is analogous to reverse hydrogenation; details are given elsewhere [203-205]. The production of ethyl acetate from renewable ethanol using the technology licensed by Kvaerner Process Technology Ltd. has been recently reported indicating that the route could be cost competitive [206,207].

2.2.5. Other routes to chemicals

Important efforts are being made for the conversion of ethanol into a wide range of hydrocarbons, e.g. gasoline and aromatics, following similar processing to the methanol case. Information of this processing can be found elsewhere [208-213].

2.3. Other platforms chemicals

As shown earlier, there is limited development of thermochemical routes via platform chemicals. To date, only methanol, DME and ethanol have been considered platform chemicals, but there are other potential compounds of interest, e.g. butanol and methane. The conversion of light hydrocarbons to high-value compounds could be one example, although these efforts are focused on the use of natural gas as feedstock. Currently research is being conducted into the efficient conversion of methane into methanol [214-216].

3. Discussion

The review provides a variety of routes via platform chemicals to be taken into account for the design of thermochemical biorefineries. However, it is still necessary to define the methods leading to these routes (they were first studied some time ago) because they could be used in a multi-production plant. For this propose, an example of design is given, based on the use of DME as a platform chemical. Since the reviewed routes were developed for the use of fossil feedstock instead of biomass and waste, the impact of the change in syngas composition needs to be clarified, e.g. in the case of natural gas as original feedstock. This and other preliminary questions for the further design of thermochemical biorefineries are introduced.

3.1. Example of thermochemical biorefinery

An example of thermochemical biorefinery based on routes via platform chemicals has been recently proposed by Haro et al. [44]. In this assessment, the DME carbonylation (see 2.1.4.) and hydrocarbonylation (see 2.1.5.) routes were selected to bring up to two sets of thermochemical biorefinery concepts. Potential products considered in that study were: methyl acetate, H_2, DME and electric power (DME carbonylation), and ethanol, H_2, DME and electric power (DME hydrocarbonylation). The study proved that concepts based on routes via platform chemicals have better or at least similar economics to BTL/G processes, despite their greater complexity [44]. In addition, a previous study [52] confirmed that the DME hydrocarbonylation route can overcome the limitation of the direct synthesis of ethanol from without a negative effect on economics [4,5,20,55,217].

3.2. Impact of feedstock selection of the mix of products

The impact of using lignocellulosic biomass or carbon-based waste instead of other fossil fuels raises two important considerations regarding the design of thermochemical biorefineries.

First, each feedstock (coal, natural gas, biomass or carbon-based waste) processing (gasification) leads to a different syngas composition, i.e. different H_2/CO molar ratios, which must be compared with the optimum H_2/CO ratio required in each route. For the single production of ethanol the optimum H_2/CO ratio would be 2 (2.1.1., 2.1.2., 2.1.3., 2.1.5., 2.1.7.), except for the *Dry Ethanol Process* in 2.1.1. (with a ratio of 0.5). For the single production of gasoline and olefins from methanol/DME (2.1.8., 2.1.9.) the ratio is also 2. However, in the case of single methyl acetate production (2.1.4.) the ratio would be 1.33, and 1 in the case of acetic anhydride (2.1.6.). Finally, in the case of ethanol as a platform chemical, only in the case of ethanol dehydrogenation to ethyl acetate (2.2.4.) the ratio would be 1.5 instead of 2. If single production is sought, then natural gas (which presents a H_2/CO ratio of 3) would be more appealing than coal, biomass or carbon-based waste as feedstock, which leads to much lower ratios in the syngas (0.5 – 1.0); and therefore, some routes via platform chemicals were intended to use natural gas according to the given description. Furthermore, the H_2 excess in the processing leads to a net production of H_2. In the case of lower H_2/CO ratios using other feedstock, the water gas shift (WGS) reaction is usually the best option to achieve enhanced conversion to products, but with an important reduction of carbon and energetic efficiency. However, as thermochemical biorefineries are focused on multi-production, a lack of H_2 could be overcome by a balanced design of the mix of co-products, i.e. what and in which amount will be produced from syngas within the thermochemical biorefinery. An example is given in 3.1., where ethanol production (which requires a ratio of 2) was compensated with DME production (which requires a ratio of 1).

Second, it seems clear that beside syngas generation and conditioning, the most important differences within the feedstock relate to availability, price and sustainable nature. These factors should be balanced by simultaneously assessing the economics and sustainability of the process. In the case of carbon-based waste, e.g. plastics, they are usually derived from crude oil so should not be classified as a neutral carbon feedstock. However, their growing volume represents a problem in landfills and recycling suffers from a technical and economic mismatch. The use of MSW in thermochemical processing may be an interesting option to be assessed. Another opportunity would be the study of co-feeding, i.e. combination of carbon neutral and other feedstock, such as plastics, natural gas or coal. Some authors have studied the subject, but further research is still necessary [219-224].

3.3. Further research on thermochemical biorefineries

In the opinion of the authors, studies on thermochemical biorefineries need common criteria for sustainability and comprehensive life cycle assessment (LCA) methodology, which include the specificity of the multi-production, fossil and waste feedstock co-feeding, and the integration of carbon capture and sequestration (CCS) technologies. The removal of CO_2 in a plant using carbon neutral feedstock would lead to negative GHG emissions, ready to be sold as CO_2 certificates. Hence, there is an opportunity in thermochemical biorefineries and common BTL/G processes to improve economics and/or fulfill sustainability if co-feeding is considered. These proposals should be performed in current and upcoming assessments of thermochemical biorefineries.

4. Conclusions

The use of recent and old-fashioned routes via a platform chemical facilitates the design of new concepts of thermochemical biorefineries. The reviewed routes demonstrate to be capable for the (simultaneous) multi-production of chemicals and fuels and therefore they serve as a keystone for the future designs of thermochemical biorefineries. Despite the lack of technoeconomic assessments based on these routes the results from a recent publication show that they could be profitable if the mix of co-products is well selected [44]. The presented routes bring a wider range of potential bio-products, both chemicals and commodities, different to those considered up to date and therefore allow more possibilities for the selection of the mix. The fact that the reviewed routes could be applied to a fossil feedstock, e.g. coal and natural gas, is a natural consequence of the concept of a thermochemical biorefinery and an advantage, since both the technology and the know-how from the processing of fossil feedstocks can be adapted and integrated in a thermochemical biorefinery. Finally, some guides for the further work on thermochemical biorefineries are given like the need of a minimum basis of agreement on LCA methodology and sustainability criteria.

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Paper 2

Technoeconomic assessment of lignocellulosic ethanol production via DME hydrocarbonylation

This paper presents the first technoeconomic assessment of a BTL plant producing ethanol via DME hydrocarbonylation. It has been published as paper in 2012[*].

1. Introduction

Bioethanol is increasingly used as a transportation fuel in USA, Brazil and Europe. It can be used pure in vehicles with modified internal combustion engines (ICEV) or blended with gasoline in regular ICEV. Nowadays, most bioethanol is produced by first generation processes based on fermentation technologies for sugar and starchy crops. However, these crops have some drawbacks: a high value for food application and low sugar yield per hectare. Thus, currently, suitable processes for lignocellulosic biomass are being developed under the name "2nd generation bioethanol processes".

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Nomenclature
ASU: air separation unit
BTL: biomass to liquid
CFB: circulating fluidized bed
HHV: high heating value
HP: high pressure
HRSG: heat recovery system generation
ICEV: internal combustion engines vehicles
LPMEOH: Liquid Phase Methanol
MEA: monoethanolamine
MESP: minimum ethanol selling price
NRTL–RK: Non–Random Two Liquids model modified with Redlich-Kwong equation of state
PEC: purchase costs for equipment
RKS–BM: Redlich–Kwong–Soave equation of state with Boston–Mathias alpha function
SMR: steam methane reformer
TIC: total installed cost

This abundant and relatively cheap biomass can be converted to ethanol by hydrolysis and fermentation (bio-chemical pathway) but also by thermochemical processing, i.e. gasification of biomass to synthesis gas (syngas) followed by catalytic synthesis or syngas fermentation. Technoeconomic studies of the direct synthesis of alcohols from syngas produced by biomass gasification have been carried out by several researchers, either based on patented catalysts [1] or expected performance of these catalysts in the future [2, 3, 4]. From the results of this research, it is clear that significant development of current mixed alcohol catalysts is needed, in terms of conversion and selectivity to ethanol, to make the process economically feasible. Indirect synthesis processes (indirect routes) could be an interesting option if they were able to achieve higher ethanol productivity so as to outweigh their inherently greater complexity.

Routes to make ethanol from syngas, through one intermediate, have been reviewed recently by Subramani [5]. This review discusses three indirect routes to ethanol: the methanol bimolecular reaction route, the methanol homologation (reductive carbonylation) route and the acetic acid route (ENSOL process) [6]. Other current indirect routes not reviewed are: indirect acetic acid route [7], Enerkem's process via methyl acetate [8, 9], dry ethanol process [10] and ethanol via dimethyl ether (DME) hydrocarbonylation [11]. Enerkem Inc. has recently developed the ethanol via methyl acetate process with a demonstration plant and two commercial plants in project or under construction [8].

In this paper, a conceptual design of a thermochemical process for the production of ethanol via DME hydrocarbonylation route is developed and economically assessed by the ASPEN PLUS process simulator. The process makes use of commercial methanol and DME synthesis technologies. No commercial DME hydrocarbonylation reactor exists today but its development is not expected to be difficult as hydrocarbonylation reaction is slightly exothermic at mild conditions (15 bar, 220 ºC), and only heterogeneous catalysts are involved.

The paper is organized as follows. First, a description of the DME hydrocarbonylation chemistry is presented which includes a short discussion of catalysts, reaction conditions and experimental kinetic data found in the literature [11, 12]. Then, the conceptual process design and modeling is described including the main design assumptions and parameters. Finally, the performance of the process is calculated for different conditions in the DME hydrocarbonylation reactor, which is modeled using the experimental kinetic data. Results of the simulation are used to assess and compare the economics of the process for each case.

2. Ethanol via DME Hydrocarbonylation Route

Recently, a new route to make ethanol from DME and syngas has been proposed [11, 12]. The innovation resides in the use of a dual catalytic bed reactor of H-Mordenite and Cu/ZnO. DME reacts with CO from the syngas to form methyl acetate in the presence of H-Mordenite catalyst (Eq. 3). Formed methyl acetate is hydrogenated to ethanol and methanol by means of the Cu/ZnO catalyst (Eq. 4).

H-Mordenite is a kind of acid zeolite that selectively catalyzes the carbonylation of DME to methyl acetate at a relatively low temperature and pressure (15 bar, 220 ºC). A great excess of CO is necessary to achieve appreciable productivities of methyl acetate due to low catalyst activity, but there is a potential for significant improvement [13]. For methyl acetate hydrogenation several metal-based catalysts could be employed [9, 14, 15, 16], such as the Cu/ZnO catalyst used in reported DME hydrocarbonylation experiments [11, 12, 17].

Table 1 shows the results obtained by Tsubaki et al. [11] using a single reactor comprised of a H-Mordenite bed in series with a Cu/ZnO bed. This single reactor produces ethanol from DME, CO and H_2. The high conversion of DME is probably caused by shifting of the carbonylation reaction by “in situ” hydrogenation of methyl acetate as soon as it is produced [11]. Table 1 also shows the effect of the CO/DME ratio on the per-pass conversion and selectivities to ethanol, methanol, methyl acetate and CO_2. As this ratio increases from 10:1 to 49:1 both per-pass conversion and ethanol selectivity increases. Thus, from a process design point of view, there would be a trade-off between ethanol productivity and syngas recirculation costs. This trade-off is economically analyzed in this paper by simulating the process for the five CO/DME ratio cases included in Table 1.

Table 1. Ethanol synthesis reactor conditions, conversion and product distribution [12].

Case Study	P (bar)	T (ºC)	H_2/CO molar ratio	DME Conversion	Selectivity of MeOH	Selectivity of EtOH	Selectivity of Methyl Acetate	Selectivity of CO_2
Ratio 10:1	15	220	1	48%	45.0%	38.0%	6.5%	10.5%
Ratio 20:1	15	220	1	55%	44.5%	39.0%	6.5%	10.0%
Ratio 30:1	15	220	1	78%	44.5%	40.5%	6.5%	8.5%
Ratio 40:1	15	220	1	83%	46.5%	41.5%	5.0%	7.0%
Ratio 49:1	15	220	1	98%	47.5%	46.0%	2.5%	4.0%

3. Process Design and Modeling

3.1. Conceptual design

Figure 1 shows the conceptual block diagram of the process. Biomass is first converted to syngas in an atmospheric circulating fluidized bed gasifier. The producer gas is cleaned-up and conditioned in order to meet the requirements of the catalysts used in the reactor network. The configuration of the reactor network is largely dictated by the way in which DME is produced in the plant. DME for hydrocarbonylation can be produced from syngas by direct synthesis or indirectly by first synthesizing methanol which is subsequently dehydrated. Based on material and energy integration issues for this specific process, the second option has been selected as it allows for the use of the dehydration reactor to convert methanol co-produced in the hydrocarbonylation reactor back to DME in order to increase ethanol production. Thus, the synthesis reactor network comprises three catalytic reactors.

As a result of the process configuration selected, the whole indirect route comprises the following set of reactions (in order of process design):

$$CO + 2H_2 \rightarrow CH_3OH \tag{1}$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{2}$$

$$CH_3OCH_3 + CO \rightarrow CH_3COOCH_3 \tag{3}$$

$$CH_3COOCH_3 + 2H_2 \rightarrow C_2H_5OH + CH_3OH \tag{4}$$

The global reaction of the direct synthesis of ethanol being:

$$4H_2 + 2CO \rightarrow C_2H_5OH + H_2O \tag{5}$$

The high global selectivity to ethanol [12] makes this indirect route very appealing, especially compared to the direct synthesis route. However, a drawback of the analyzed route is the high excess of reactant (CO) needed to achieve a relatively high per-pass conversion of DME.

Another advantage of this indirect route is that separation of ethanol-water mixtures is not necessary as water is not co-produced with alcohols in the same reactor, which occurs in the direct synthesis of ethanol. This results in energy savings for distillation because the dehydration of ethanol is not necessary. Water is only generated in the DME synthesis reactor but this is not a problem as water can be easily separated from DME before feeding DME to the hydrocarbonylation reactor, preventing deactivation of H-Mordenite by water [11, 12, 13]. The methyl acetate produced in the hydrocarbonylation reactor is recycled to the reactor where it is assumed to be hydrogenated to methanol and ethanol.

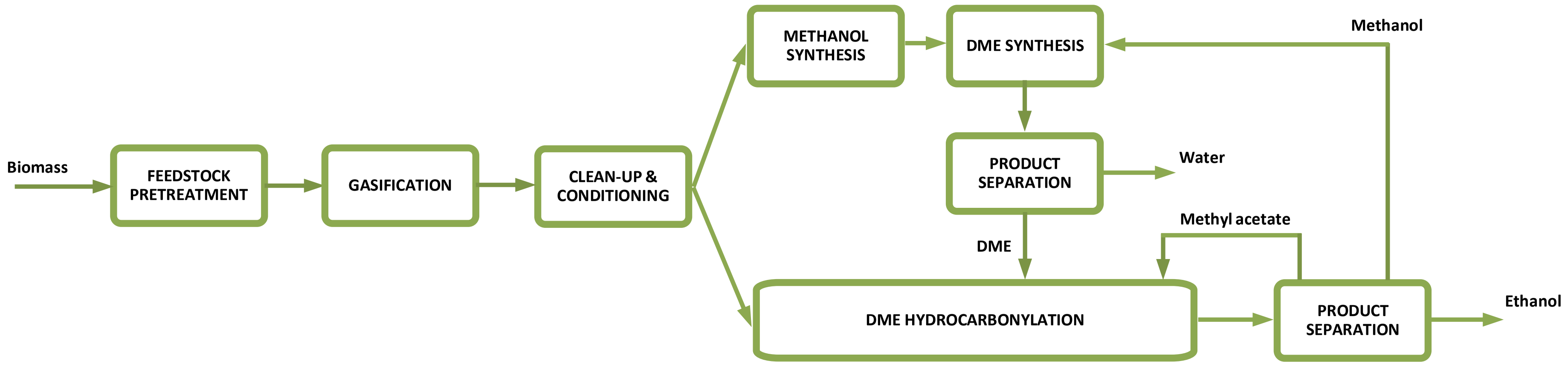

Figure 1. Scheme of ethanol via DME hydrocarbonylation route.

3.2. Process description and modeling

Figure 2 shows a block diagram of the process. As a design basis, a plant size of 2140 dry tonnes/day of poplar chip (500 MW_{HHV}) was selected. This plant size is very similar to that selected in other BTL plant assessments [2, 3, 4, 18], allowing for direct comparison with results obtained in these studies. Below, each process area is briefly described and the modeling approach is presented.

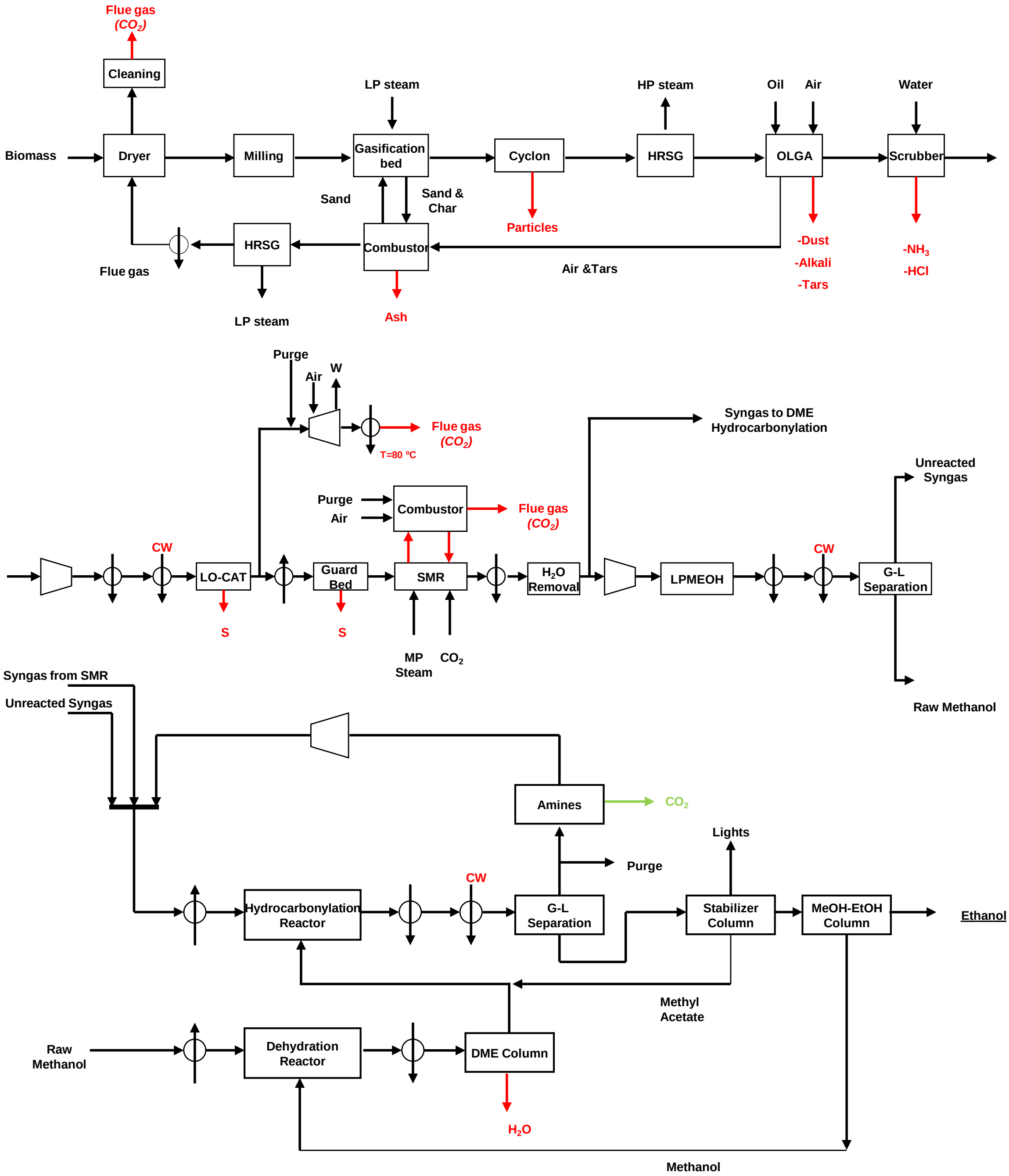

Figure 2. Process block diagram.

3.2.1. Feedstock pretreatment

Poplar chip is delivered to the plant gate with 30 wt% moisture and dried in a rotary dryer, where moisture content is reduced to 12 wt% with combustion gases from the indirect circulating fluidized bed gasifier. The combustion gases are previously cooled down to 450ºC in an HRSG, where HP steam is generated. This temperature is selected in order to obtain a flue gas temperature of 150°C at the outlet of the rotary dryer, ensuring good dispersion of the plume. Dried poplar chips are sent to a hammer mill for size reduction under 4 cm. The ultimate analysis of poplar chips feedstock is given in Table 2.

3.2.2. Gasification

Gasification can take place at different pressures, by direct or indirect heating and oxygen or air. For the synthesis of liquid fuels a non-diluted syngas with nitrogen is preferred. This leads to three gasifier alternatives: (a) a pressurized entrained flow gasifier operated with oxygen, (b) a pressurized or atmospheric CFB (circulating fluidized bed) operated with oxygen/steam and (c) an atmospheric-pressure indirect CFB gasifier operated with air/steam. An atmospheric indirectly-heated CFB is selected because it does not require an Air Separation Unit (ASU), which would consume a significant amount of power [2]. The gasifier is modeled using correlations (a non-equilibrium model) based on experimental data from the Battelle Columbus Laboratory gasifier as reported by [19]. The gasifier performance for the selected operating conditions is shown in Table 3.

3.2.3. Gas Clean-up and Conditioning

The syngas from the gasifier contains dust, tars, nitrogen and alkali compounds and halogens which must be removed in order to prevent damage to equipment and the poisoning of catalysts downstream. First, particulates are partially removed by high-temperature cyclones. Next, tars and the rest of particulates are removed using a wet scrubbing system with organic dissolvent (OLGA^{TM}) [20]. Collected tars are recycled to the combustor of the indirect CFB gasifier. Nitrogenous compounds, alkalis and HCl are removed by consecutive scrubbers. The resulting stream is compressed to 17 bar and desulfurized in a liquid phase oxidation process (LO-CAT) where H_2S is oxidized to elemental sulfur. The LO-CAT process was selected because it is appropriate to treat gases with low H_2S content and does not remove CO_2, which is needed in the steam reformer as explained below [21, 22]. The concentration of H_2S and total organic sulfur compounds in the outlet stream is decreased to ppbv levels by hydrogenation of organic sulfur compounds and further H_2S removal in a Co-Mo/ZnO dual bed. This guard bed also hydrogenates olefins to parafins which are easier to reform. At the inlet of the Co-Mo/ZnO dual bed a fraction of the partially cleaned gas is diverted to the power plant in order to satisfy the energy self-sufficient criteria.

The desulfurized syngas enters a steam methane reformer (SMR) where methane and light parafins are converted into syngas. CO_2 must be fed into the steam methane reformer in order to get a H_2/CO molar ratio equal to 1 at the hydrocarbonylation reactor inlet (H_2/CO ratio of hydrocarbonylation experiments, Table 1). However, that would require a large recirculation of CO_2 from the Amine unit located in the hydrocarbonylation loop. There is an economic trade-off between large-scale CO_2 recycle and performance of the hydrocarbonylation reactor, which cannot be evaluated due to the lack of experimental kinetic data for different H_2/CO ratios. Relatively low CO_2 recycle was considered resulting in H_2/CO ratio between 1.2 and 1.55 at the hydrocarbonylation reactor inlet. The implications of this decision are explained in the DME hydrocarbonylation loop section. The reformed gas is dehydrated in a molecular sieve, preventing the presence of water in the DME hydrocarbonylation reactor. A fraction of the reformed syngas is sent to the hydrocarbonylation loop while the rest is sent to the methanol synthesis reactor. The split fraction to the hydrocarbonylation reactor ranges from 0.4 to 0.6 depending on the desired CO/DME operating ratio.

Table 2. Ultimate analysis of biomass feedstock (poplar chip).

Component	% wt, dry basis
Carbon	50.90
Hydrogen	6.05
Oxygen	41.92
Nitrogen	0.17
Sulfur	0.04
Ash	0.92
Moisture	30% wt
HHV (d.b)	20.18 MJ/kg

Table 3. Gasifier operating parameters, exit gas composition and efficiency.

Gasifier Performance	
Pressure	1.5 bar
Temperature	900 ºC
Steam (2 bar, 140ºC)/dry Biomass ratio	0.4
Heat loss in gasifier	1.53% HHV
Cold gas efficiency (%HHV)	77.07
Component	Mole (%)
H_2	14.55
CO	23.64
CO_2	6.92
H_2O	43.43
CH_4	08.43
H_2S	184 ppm
NH_3	0.18
Tars	0.15
Lights	2.70

3.2.4. Methanol synthesis

The syngas feed to the methanol reactor is compressed to 50 bar and heated to 235ºC. There is a wide variety of commercial methanol synthesis technologies that can be selected for this application. However, this analysis is based on a Liquid Phase Methanol (LPMEOH) reactor modeled with data from the Kingsport LPMEOH™ CCT Project [24, 23]. This slurry type reactor is able to process CO rich syngas and achieves high per-pass conversion to methanol, so that no recirculation of unconverted syngas is needed. Besides, the liquid phase methanol reactor is flexible in terms of feed composition which is advantageous as the H_2/CO ratio of the reformed syngas only needs to be adjusted to satisfy the requirements of the hydrocarbonylation reactor. The once-through operation allows enough methanol production for the DME synthesis step. The output stream of the methanol reactor is cooled down to 45ºC for methanol recovery but also most of the water co-produced. The off-gas stream from the gas-liquid separator comprises unreacted syngas, and small quantities of methanol, DME and traces of water. The off-gas is expanded down to the hydrocarbonylation reactor pressure in a turboexpander, and then sent to the hydrocarbonylation synthesis loop.

3.2.5. DME hydrocarbonylation loop

The feed to the hydrocarbonylation reactor is a mixture of five gas streams: (a) clean and conditioned syngas fraction from SMR, (b) off-gas from the methanol synthesis area, (c) unconverted syngas from the hydrocarbonylation reactor, (d) DME from the methanol dehydration reactor and (e) recycled by-products of the hydrocarbonylation reactions (mixture of methanol/methyl acetate). Streams (d) and (e) contain small amounts of methanol and ethanol. In the hydrocarbonylation reactor it is widely considered that recycled methanol and ethanol behave as inerts while recycled methyl acetate is completely hydrogenated [9, 11, 12, 14, 15, 16]. As previously mentioned, in the simulations, the H_2/CO ratio at the inlet of the hydrocarbonylation reactor (see Table 4) is larger than the H_2/CO ratio of the hydrocarbonylation experiments (Table 1). Based on a recent study [25], the H_2/CO ratio does not affect the conversion of DME in the carbonylation bed. However, a larger H_2/CO ratio will probably result in higher methanol production from CO in the hydrogenation bed. This is not a critical problem as methanol is recycled and converted back into DME and the global productivity will not dramatically change. Nonetheless, it is recognized that a larger methanol recycle will also increase capital and operating costs. Therefore, there is an optimum setting for the H_2/CO ratio which minimizes the total cost of recycling CO_2 to the SMR and methanol to the dehydrator. The optimum H_2/CO ratio cannot be determined due to the lack of hydrocarbonylation experiments at different H_2/CO ratios. As an approximation, we have assumed that the product distribution does not change with the H_2/CO ratio. Regarding the configuration of the reactor, the simulations show that the adiabatic ΔT is close to common methanol synthesis reactors, so similar reactor designs would be suitable.

The reactor effluent is cooled down to 35ºC with cooling water. A knock-out vessel is used to separate unconverted syngas and DME from condensed products with reasonable ethanol recovery (nearly 80%). In order to avoid a build-up of CO_2 concentration in the synthesis loop an amine scrubber using monoethanolamine (MEA) is employed. However, a purge is necessary in order to prevent methane build-up in the hydrocarbonylation loop (10% v/v methane as design limit).

3.2.6. Products separation

The condensate from the gas-liquid separator of the hydrocarbonylation loop is processed in a stabilizer column with a partial condenser. The vapor distillate which contains the dissolved gases (mainly CO_2 and CH_4) is recycled to the burners of the SMR. The liquid distillate contains 98% of the incoming methyl acetate diluted with methanol, ethanol and traces of DME. This stream is recycled to the hydrocarbonylation reactor to achieve total methyl acetate conversion. The bottom stream recovers 95% ethanol and 80% methanol. This stream is depressurized and enters into a column distillation where methanol is recovered as distillate while ethanol is recovered as bottom stream. Methanol is sent to the dehydration reactor to produce more DME. The ethanol product satisfies ASTM specifications for automotive spark-ignition engines.

3.2.7. Methanol dehydration and byproducts recycle and conversion

The methanol synthesized in the LPMEOH reactor and co-produced in the hydrocarbonylation reactor are dehydrated to DME in a fixed-bed reactor. The dehydration reaction can take place on different solid-acid catalysts such as γ-alumina, modified-alumina with silica and phosphorus, Al_2O_3–B_2O_3 and molecular sieve materials (chabazites, mordenites, SAPOs, etc.), in a temperature range of 250–400 ºC and pressures up to 20 bar [26, 27]. In this study, we have selected modified γ-alumina, which has shown good stability and is widely employed by companies such Air Products and Toyo Engineering Corporation. For this analysis, we used typical Toyo dehydration conditions, i.e. conversion of 85% and almost 100% selectivity to DME [27]. The gas outlet stream from the dehydration reactor is cooled down and fed to a distillation column to obtain a DME rich overhead stream and an aqueous bottom stream. This stream is sent to the water treatment area which is not modeled here but is included in the economic assessment.

3.2.8. Energy Integration and Balance

As previously mentioned, all cases were designed to be both energy self-sufficient and “electrical energy neutral”. First, the heat exchanger network is designed manually by matching close hot and cool streams whenever possible. A minimum temperature difference of 20 ºC, 30ºC and 40 ºC are considered for liquid-liquid, liquid-gas and gas-gas heat exchanges, respectively. The main heat sources for high pressure steam generation are the outlet of SMR, raw syngas from the gasifier and the flue gas from the char combustor. The power demands of the plant are completely satisfied by diverting some cleaned-up syngas to a combined cycle as shown in Figure 2. The main heat sinks of the process are the boilers of the distillation columns and amine unit, and hydrocarbonylation loop preheaters.

The modeling of process units is summarized in Table 4.

Table 4. Modeling of main process units.

	Parameter	Value
Heat Exchangers	Pressure drop	3 psi
Pumps	Mechanical Efficiency	0.90
Compressors	Isentropic efficiency	0.78
	Max. pressure ratio	3.5
Process Turbines	Isentropic efficiency	0.72
Gas Turbine	Isentropic efficiency	0.90
	Pressure	49 bar
	Temperature	250ºC
	CO per-pass conversion	30.76%
Methanol reactor [23, 31]	CO_2 per-pass conversion	8.90%
	Selectivity to MeOH	89.15%
Modeled as a RStoic	Selectivity to H_2O	10.57%
	Selectivity to DME	0.14%
	Selectivity to methane	0.14%
	H_2/CO ratio	1.70
	Pressure drop	3.3 bar
		10:1 1.57
Hydrocarbonylation reactor	H_2/CO ratio	20:1 1.52
	(for each CO/DME	30:1 1.34
Modeled as a RStoic (see Table 1 for conversion, selectivities and operating conditions)	ratio)	40:1 1.53
		49:1 1.29
	Pressure drop	10 psi
	Pressure	20.2 bar
	Temperature	320 ºC
	MeOH per-pass conversion	85%
Methanol Dehydration reactor [27]	EtOH per-pass conversion	80%
	Selectivity to DME	100%
Modeled as a RStoic	Selectivity to C_2H_4	100%
	% v/v ethanol in feed	0.2%
	% v/v H_2O in outlet stream	44.9%
	Pressure drop	10 psi

3.3. Thermodynamic Modeling

Two thermodynamic models have been used for process simulation. For gasification, and gas clean-up and conditioning areas, the equation of state of Redlich–Kwong–Soave with Boston–Mathias alpha function (RKS–BM) is employed, whereas the NRTL–RK model is employed in methanol synthesis, DME hydrocarbonylation, methanol dehydration and product separation areas. These thermodynamic models for process simulation were chosen according to recommendations from the literature [28] and ASPEN PLUS documentation. For the NRTL model, binary parameters for DME-water, DME-methyl acetate and DME-ethanol mixtures are taken from the literature [29, 30].

4. Process Economics

Results from the process simulations were used to estimate capital and operating costs. Purchase costs for equipment (PEC) are taken from published BTL studies and vendor quotes. First, the purchase costs are scaled and the effect of inflation is corrected by using the CEPCI (Chemical Engineering Plant Cost Index) index. Then, the installed equipment cost is calculated by multiplying the purchase cost by an installation factor. If the installation factor is unknown it is assumed 2.47 according to Table 5. Thus, the total installed cost (TIC) is calculated by adding up the cost of the individual equipment. The indirect costs are estimated as percentages of TIC as shown in Table 6. The expected accuracy of estimate is ±30%, typical of a study estimate [34].

Finally, the operating costs are calculated according to Table 7. Fixed operating costs are calculated as a percentage of TIC while variable operating costs are calculated based on the cost of the consumables.

Once the capital and operating costs are calculated, the minimum ethanol selling price is calculated as the ethanol price which makes the net present value of the project zero with a 10% rate of return. The economic parameters used for the discounted cash flow analysis are shown in Table 8.

Table 5. Data for capital cost calculations of the most important equipment.

Unit	Base purchase cost (MM$)	Reference year	Scale factor (n)	Units	Base Scale	Installation factor	Reference
Indirectly-heated biomass gasifier	27.3	2008	0.70	dry tonne biomass/day	550	1	supplier
OLGA	-	-	-	-	-	-	confidential
Syngas compressor	5.85	2009	0.70	MW_e	5.44	1.32	supplier
LO-CAT	1.0	2002	0.65	lb sulphur/hour	108	2.47	[2]
SMR	41.0	2002	0.60	kmol total reformed/hour	1,277	1	[32]
Amine CO_2 capture system	15.4	2001	0.65	lb CO_2/hour	100,203	2.47	[33]
LPMEOH reactor	5.1	2002	0.60	tonne methanol/hour	18.9	2.10	[23]
Gas turbine and Combustor	19.09	2003	0.70	MW_e	26.3	1	[18]

Scaling equation: $Cost/Cost_{base}= (Scale/Scale_{base})^n$.

The installation factor is 1 if the base cost already includes the indirect costs.

Table 6. Cost factors for estimating direct and indirect costs as a percentage of purchase cost equipment (PEC) and total installed cost (TIC), respectively.

Direct Cost	% PEC
Purchase equipment installation	39
Instrumentation and control	26
Piping	31
Electrical systems	10
Building (including services)	29
Yard improvements	12
Total direct costs	147
Indirect Costs	**% TIC**
Engineering design and procurement	7.9
Contractor Management and control	2.2
Capital spares and other costs	2.0
Operator training	1.0
Start up assistance	1.0
EPC constructor contingency	15.0
Total indirect costs	29.1

Table 7. Data for calculating operating costs.

Fixed operating costs	% TIC
Labor	1.56
Maintenance	1.50
General expenses	3.07
Management and operation services	0.44
Cost of Goods Sold- Marketing, Logistics and others	1.32
Insurance	0.50
Total	8.39
Variable operating costs	
Biomass (USD/dry tonne)	66
SMR catalyst (USD/kg)[a]	10.30
LPMEOH catalyst (USD/L methanol)	0.0044
Hydrocarbonylation catalyst (USD/L ethanol)[b]	0.0044
Lo-Cat Chemical (USD/kg sulfur produced)	0.15
Waste water (USD/m^3)	0.731
Boiler chemicals (USD/tonne)	0.12
Water demineralization (USD/tonne)	0.34
Ash disposal cost (USD/tonne)	29.02

[a] GSHV (standard conditions) =1780 h^{-1}, 25% catalyst replacement per year, catalyst density = 910 kg/m^3.

[b] assumed (no better data available).

Table 8. Economic assumptions for discounted cash flow analysis. Working capital and cost of land are recovered at the end of plant life.

Parameter	Value
Rate of return	10%
Debt/Equity	0/100%
Plant life	20 years
Depreciation (Linear)	10 years
Salvage value	0 M USD
Construction period	1 year
Income tax	30%
Working capital	1-month operating costs
Land	6% TIC

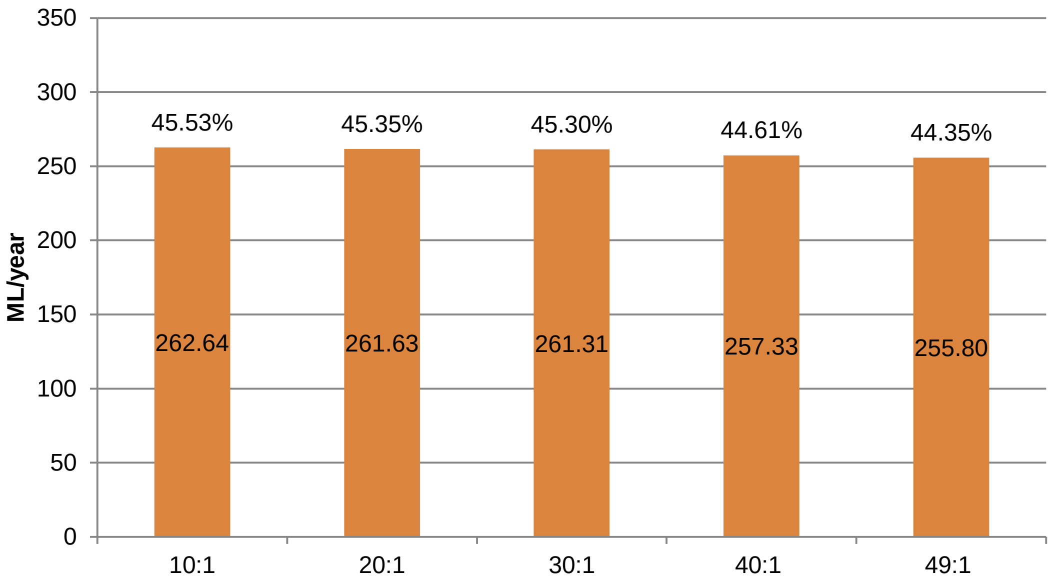

Figure 3. Ethanol production and Biomass to Ethanol efficiency (% HHV) for evaluated cases.

5. Results and Discussion

5.1. Process discussion: material and energy balance results

Figure 3 shows that ethanol production varies from 255.8 for 49:1 case up to 262.6 ML/year for 10:1 case (a variation of only 2.6%), or equivalently, energy efficiency of biomass to ethanol ranges from 44.35 to 45.53 % (HHV basis). The ethanol production is very similar for all cases despite differences in DME conversion and ethanol selectivity for different CO/DME ratios. These results also prove that using a H_2/CO ratio different from 1 in the hydrocarbonylation reactor does not affect global productivity. First, it must be taken into account that the global selectivity to ethanol is theoretically 100%, irrespective of selectivity to ethanol in the hydrocarbonylation reactor, as methanol co-produced in the reactor is recycled to be converted back into DME while methyl acetate is also recycled to be hydrogenated into ethanol. The reason why ethanol productivity decreases with the CO/DME ratio is that the amount of syngas used to satisfy the power demand increases, diminishing the syngas available for ethanol production. The power demands of the plant are shown in Figure 4. As the CO/DME ratio increases the power demands of the plant increase due to larger power consumption in the compressors of the hydrocarbonylation loop and methanol area. Therefore, we can conclude that there is no benefit in achieving large per-pass conversion of DME by operating with large CO/DME ratios, from an energy point of view.

5.2. Economic results

As shown in Figure 5, the minimum ethanol selling price (MESP) increases with the CO/DME ratio from 0.555 to 0.592 USD_{2010}/L. Therefore, as previously mentioned, a low CO/DME ratio is economically favored despite of low DME per-pass conversion and selectivity to ethanol. These results are currently not competitive. The current US market price of corn fuel ethanol is 0.45 USD_{2010}/L [35] and in Europe bioethanol prices are approximately 0.67-0.69 USD_{2010}/L [36].

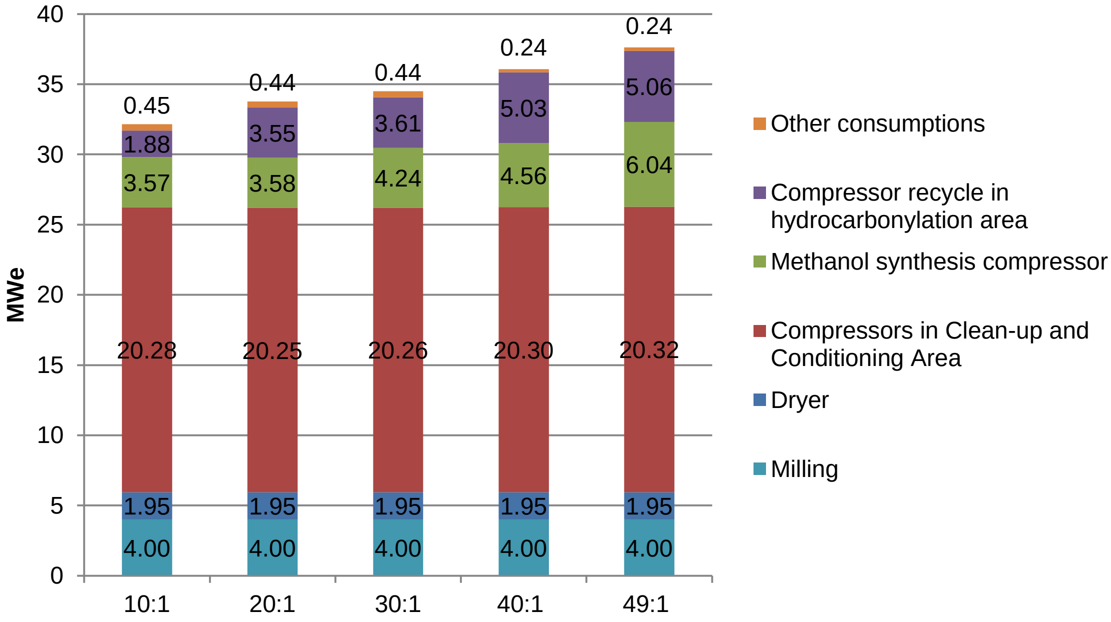

Figure 4. Electrical power consumption for each CO/DME ratio.

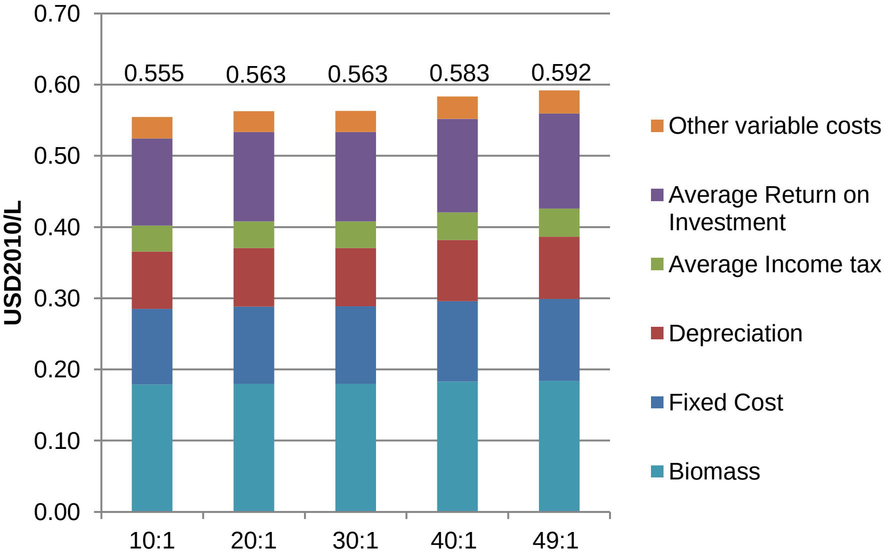

Figure 5. Ethanol Production cost for each case. Other variable costs include all variable costs except biomass costs.

The break-down of MESP in Figure 6 shows that in all cases, the MESP is equally distributed between the operating costs (biomass, fixed costs and other variable costs) and recovery of the investment (depreciation and return on total investment). The biomass cost and fixed costs are the most important operating costs (Figure 6) and each of them equally contributes to the MESP. Catalyst costs only account for about 4-6% of the total operating cost, since this process uses inexpensive commercial catalysts.

Figure 7 shows that fixed capital cost increases from 332.56 to 352.12 M USD_{2010} as CO/DME ratio increases from 10 to 49. Biomass pretreatment and gasification, and gas clean-up and conditioning account for 45-50% of the fixed capital cost. The synthesis area (methanol, DME and hydrocarbonylation) and CO_2 capture system account for 22% of the fixed capital cost. The fixed capital cost increases with CO/DME ratio because of the increase in the cost of the power island, which is a consequence of the larger power demands of the plant.

A sensitivity analysis of ethanol price (MESP) to biomass price (±60%, i.e. from 30 to 100 USD/dry tonne) and total investment cost (±30%) has been carried out as there is an important uncertainty in both costs. Ethanol price would vary ±0.1 USD/L (Figure 8), irrespective of the CO/DME case. The same variation of ethanol price occurs for a ±30% change in TIC (Figure 9), indicating that the ethanol price is more sensitive to TIC than to biomass price. Despite of the uncertainty, the MESP is close to ethanol market prices in Europe.

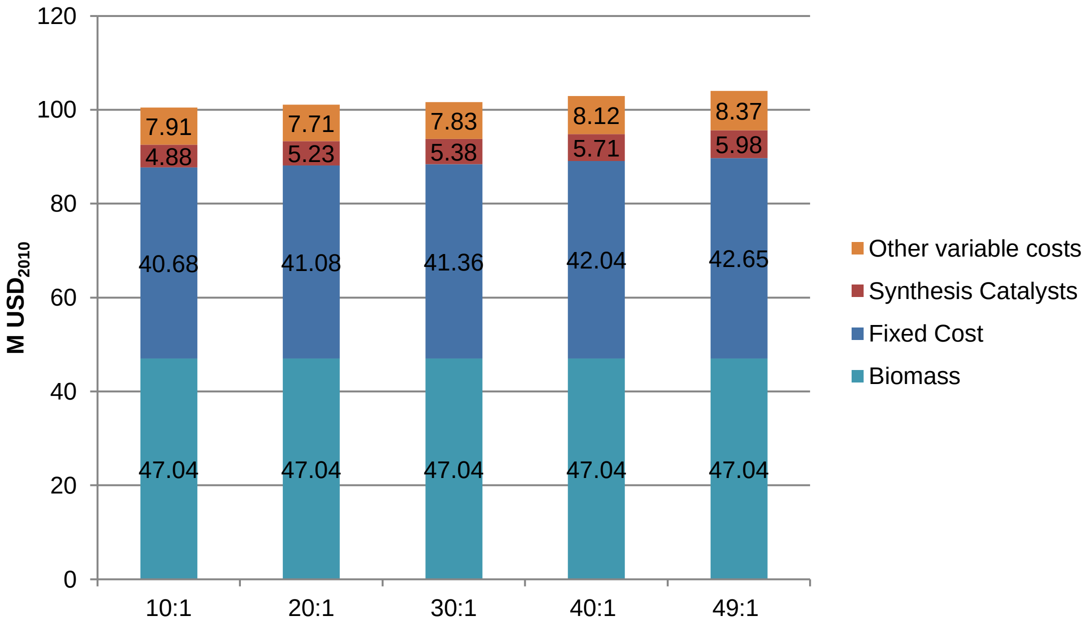

Figure 6. Break-down of operating costs for each case. Other variable costs include all variable costs except biomass and synthesis catalyst costs.

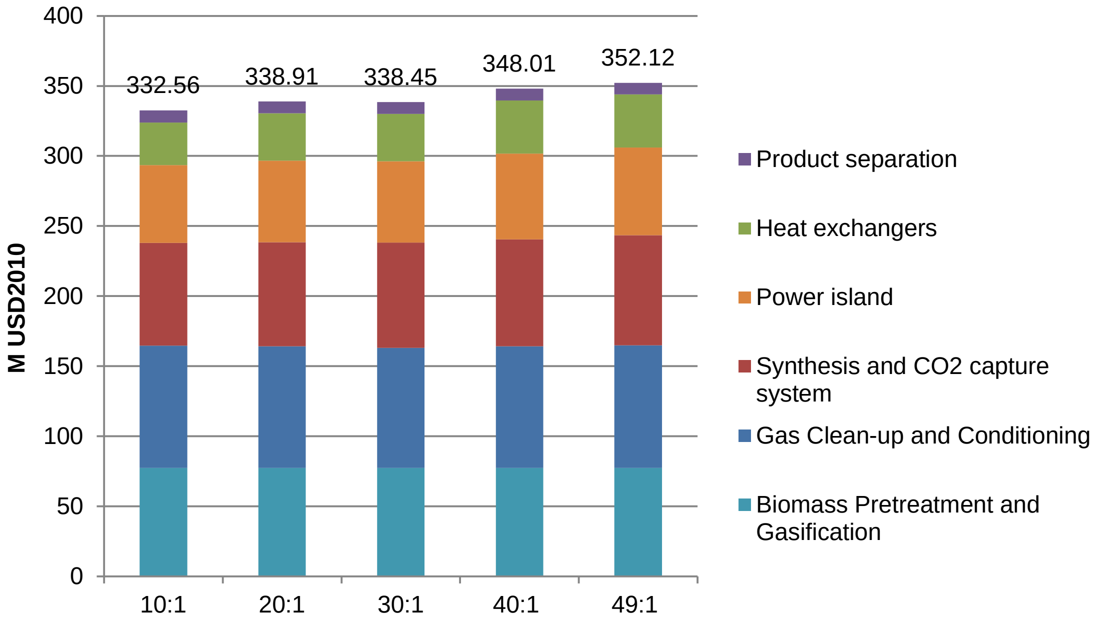

Figure 7. Break-down of fixed capital costs for each case. Note: land cost is not included.

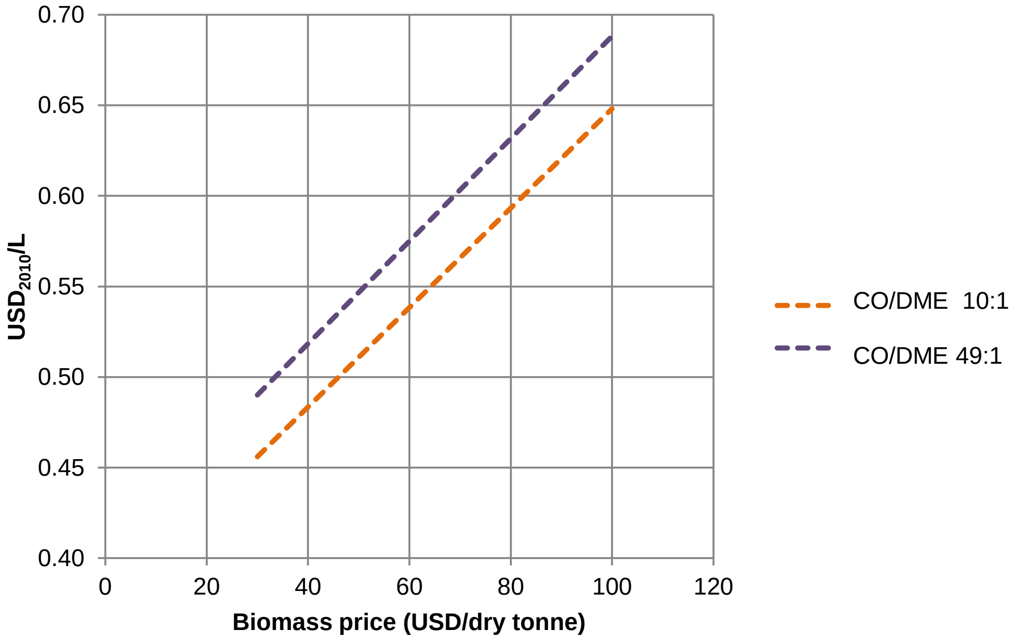

Figure 8. Sensibility analysis of MESP to biomass price for the largest and lowest CO/DME cases. Biomass price for base case is 66 USD/dry tonne.

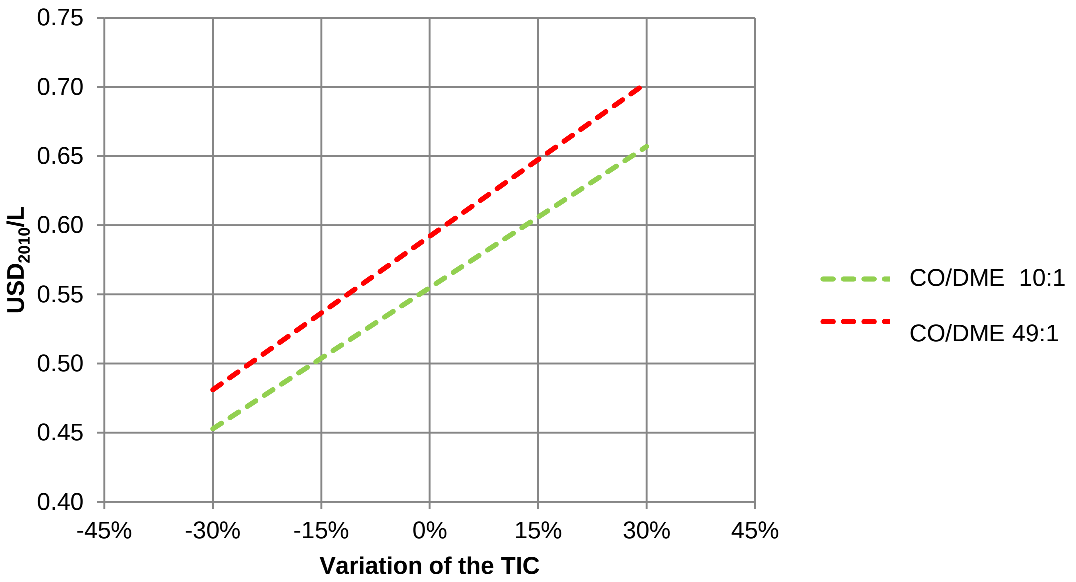

Figure 9. Sensibility analysis of MESP to a ±30% uncertainty in investment costs for the largest and lowest CO/DME cases.

5.3. Comparison with other bioethanol routes

Table 9 compares the result of this work with other studies on thermochemical [2] and biochemical [37] processes to produce ethanol from lignocellulosic biomass. In these studies, the processes are designed to be energy self-sufficient and the economic assumptions are similar to this work (10% rate of return, 20 year plant life). MESP for the DME hydrocarbonylation process is lower than “state of the art” 2^{nd} generation biochemical processes. NREL (National Renewable Energy Laboratory) assessments of a targeted (i.e. non-existent) synthesis catalyst and tar reformer catalyst for the thermochemical direct route show lower production costs than the proposed indirect route. The main reason for this is the great improvement in the performance of direct synthesis catalysts assumed by NREL and also their much lower biomass price and equipment costs. For instance, if feedstock price assumed by NREL were used in our assessment, the MESP for the hydrocarbonylation route would decrease from 0.555 to 0.515 USD_{2010}/L (7.2% reduction). For this reason, a direct comparison with NREL’s works is unfair as two different scenarios (present and future) and biomass price are considered.

6. Conclusions

This technoeconomic assessment shows that the production cost of ethanol via the DME hydrocarbonylation route is lower than that reported in the literature for the production of lignocellulosic ethanol via biochemical pathway [37]. Thus, ethanol from the DME route looks promising. This study has raised some important issues with regard to catalyst performance which should be investigated in order to optimize the design of the process such as performance of the hydrocarbonylation catalyst at different H_2/CO ratios.

As compared with the "state of the art" biochemical synthesis route, the ethanol production cost via the DME hydrocarbonylation route is lower because its larger energy efficiency and selectivity to ethanol outweigh its complex configuration. Hence, the thermochemical ethanol production via the DME hydrocarbonylation route could be cost-competitive in the near future.

Table 9. Comparative results from this study with other comparable thermo and biochemical processes. All data are up-to-date and refer to 2010.

	This work	**NREL (CFB+ targeted MoS_2 synthesis catalyst) [2]**	**2nd Generation biochemical [37]**
Feedstock price (USD/dry tonne)	87[a]	51	87
Plant size (dry tonne/day)[b]	2140	2000	2000
Ethanol production (ML/year)[c]	263	234	202
Export of electricity (MWe)[d]	0	0	25.8
Total Capital Investment (M USD)[e]	434.1	252.4	395
Extra revenues (M USD/year)[f]	0	42	12.3
Net operating costs (M USD/year)[g]	97.1	81.9	124.5
MESP (USD/L)	0.613	0.353	0.95
Biomass to ethanol efficiency (%HHV)	45.53	47.4[h]	-

[a] For comparison proposes, the 10:1 case has been updated with a 87 USD_{2010}/dry tonne price.

[b] Biomass feedstock for biochemical processing is corn stover (25% moisture); other: poplar chips (30% moisture).

[c] 8000 operating hours per year for DME process; other: 8406.

[d] Sold to grid, 5.7 cent/kWh credits for electricity.

[e] Including working capital.

[f] Revenues from electricity or co-products.

[g] Fixed and variable operating costs less revenues from electricity or co-products.

[h]. Efficiency to total alcohols

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Paper 3

Technoeconomic assessment of potential processes for bio-Ethylene production

This paper presents a technoeconomic assessment of different pathways for the production of bio-ethylene using bioethanol or DME as platform chemical, including the BECCS (BioEnergy with carbon capture and storage) concept. It has been published as paper in 2013[*].

1. Introduction

The production of plastics from a renewable feedstock is of great interest nowadays. The use of biomass and carbon-based waste in the production of plastics can contribute to the depletion of greenhouse gas (GHG) emissions and secondarily to partially fulfill the growing demand for plastics expected in the near future. There are several renewable feedstocks for plastic production [1], but only a limited number of petrochemical commodities could be produced from biomass using commercial or potential commercial technologies. These commodities are ethylene, propylene and BTX (benzene, toluene and xylenes) [1], which can be easily introduced in current petrochemical facilities. However, regarding both the plastic market and processing of biomass, bio-ethylene seems a reasonable medium-term target. Two reasons support this position: first, ethylene is by far the largest-volume commodity of the three mentioned above; and second, it can be produced by available or demonstrated technologies, such as the dehydration of ethanol or methanol(DME)-to-olefins [2]. Currently, the main use of ethylene is the production of plastics (via polyethylene or vinyl acetate) [2].

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[*] Haro P, Ollero P, Trippe F. Technoeconomic assessment of potential processes for bio-Ethylene production. *Fuel Process Technol*. 2013;114:35-48. DOI: 10.1016/j.fuproc.2013.03.024

Nomenclature

BECSS: bioenergy with carbon capture and storage

BETE: bioethanol-to-ethylene

BTL: biomass-to-liquid

BTX: benzene, toluene and xylenes

CCS: carbon capture and storage

DME: dimethyl ether

GHG: greenhouse gas

HHV: high heating value

IEA: International Energy Agency

LPG: liquefied petroleum gas

RKS–BM: Redlich–Kwong–Soave with Boston–Mathias modifications

WWT: waste water treatment

The price of ethylene is being highly dependent on the price of crude oil (see Figure 1), since half the price of ethylene is due to the feedstock (crude oil) cost [2]. Hence, the production costs of plastics, which in general use petrochemical commodities like ethylene as source, are related to the evolution of crude oil price and therefore suffer from its volatility. The introduction of biomass as a secondary or alternative feedstock would have two positive effects from an economic point of view. On the one hand, it would reduce the dependence on crude oil prices, whose evolution has fluctuated dramatically in recent years. On the other hand, it would improve industrial development in regions without natural fossil sources, but with a relatively high capacity for biomass production.

From a sustainable point of view, the potential of GHG reductions inherent in the use of biomass as a renewable carbon feedstock can be enhanced by using carbon capture and storage (CCS). This option has been recently proposed by the International Energy Agency under the BECCS (Bioenergy with Carbon Capture and Storage) concept [3]. The storage of CO_2 with a renewable or *green* origin allows for the possibility of selling the amount of CO_2 sequestrated via CO_2 credits (emissions trading).

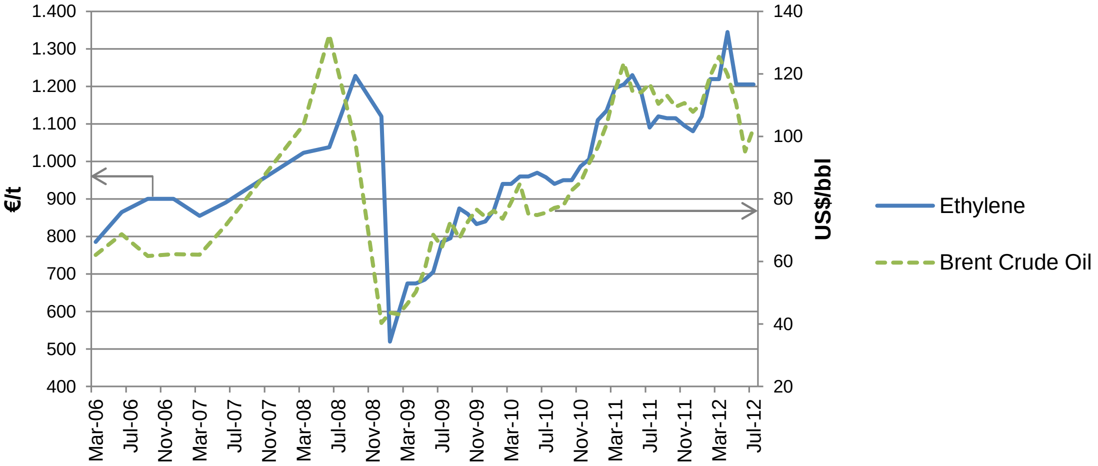

Figure 1. Ethylene contract bulk price and Brent Crude Oil price evolution from 2006 to 2012 (data taken from [4, 5]).

The aim of this work is to study the technical and economic feasibility of different alternatives to produce bio-ethylene from biomass and to assess the possibility of extra revenues with the integration of BECCS into the processes. To date there is no published work in the literature focused on the study of bio-ethylene production and the comparison of different alternatives. Another contribution of this study is the consideration of BECCS and the possibility of extra revenues from CO_2 emissions trading.

The considered alternatives for the production of bio-ethylene are shown in Table 1 and Figure 2, and represent the current most promising routes for ethylene production from biomass. In the first set of alternatives, ethanol is the selected platform chemical for the production of ethylene (via dehydration). As ethanol can be produced from biomass by using different processes, the most representative and innovative have been included, i.e. 1st generation bioethanol, 2nd generation bioethanol via enzymatic hydrolysis and syngas fermentation, and 2nd generation bioethanol via thermochemical processing. In the case of bioethanol via thermochemical processing, both the conventional syngas processing (direct route) [6] and also an innovative process recently assessed (indirect route) with promising results [7] are included. In the second set, ethylene is produced along with other olefins, mainly propylene, using DME as the platform chemical. In this process, DME is catalytically converted into hydrocarbons and it has been recently evaluated in a previous study [8].

2. Description of the case studies

This section provides an outline of the five case studies (see Table 1 and Figure 2), including a summary of the technology involved, process design and system boundaries for the modeling. The section is divided into two blocks accounting for alternatives using ethanol as a platform chemical and that using DME.

2.1. Case studies involving ethanol dehydration (case studies 1-4)

In case studies 1-4 the ethanol input for the dehydration plant is assumed to be commercial fuel grade or anhydrous ethanol. Hence, ethanol processing is the same regardless of the considered case study. For case studies 1 and 2, the plant capacity is not restricted and they are assessed for a range of plant capacities. For case studies 3 and 4 the production of ethylene is assumed to be integrated with ethanol synthesis using the process designs of the previous studies. Hence, the plant capacity in these cases is fixed. Possible alternatives for the modeling of case studies 1-4 are given in section 5.1.

2.1.1. Case study 1: 1st generation ethanol

Despite the controversy surrounding the use of food-competitive feedstock, there is a great interest in the valorization of 1st generation ethanol to high-value products. Production of ethylene was one of the first examples, e.g. the BETE (BioEthanol-To-Ethylene) process in the 1980s [12]. The relatively low-cost of 1st generation ethanol in Brazil [9], along with the increasing price of crude oil, triggered the interest in the use of ethanol as a platform chemical [2, 13].

Despite 1st generation ethanol representing an appealing option for ethylene production, the optimal capacity of the dehydration plant is still uncertain. Typical sizes of new ethanol plants are about 300–500 ML/year [9], whereas the average size of an ethanol plant in Brazil is about 50 ML/year [2]. This wide range of plant capacities leads to an equivalent range of ethylene production capacities if a *one-to-one* strategy is followed, i.e. the dehydration plant is fed with the production of a single ethanol plant. However, Braskem S.A. has recently put a combined dehydration-polymerization plant into operation with a capacity of 200 tonnes/year of polyethylene and ethanol consumption of 462 ML/year [14]. The size of Braskem's plant suggests that the *one-to-one* strategy is inappropriate. The selected capacities used in this assessment range from 150 to 500 ML/year (118–395 tonnes/year) of ethanol. In this study, we consider the most relevant sources for commercial ethanol, i.e. EU, USA and Brazil.

Table 1. Summary of studied cases for ethylene production from biomass.

Case study	Technology	Platform chemical	Status	Reference
1	Dehydration	1st generation ethanol	Already commercial	Comercial bioethanol from EU, USA and Brazil [9]
2		2nd generation biochemical ethanol (enzymatic hydrolysis) & ethanol via syngas fermentation	Close to commercial introduction	Kazi et al. [10] Fornell et al. [11]
3		2nd generation ethanol (thermochemical, direct route)	In advanced stage of development	Villanueva et al. [6]
4		2nd generation ethanol (thermochemical, indirect route)	In a first stage of development	Haro et al. [7]
5	MTO	DME	Close to commercial introduction or already commercial	Haro et al. [8]

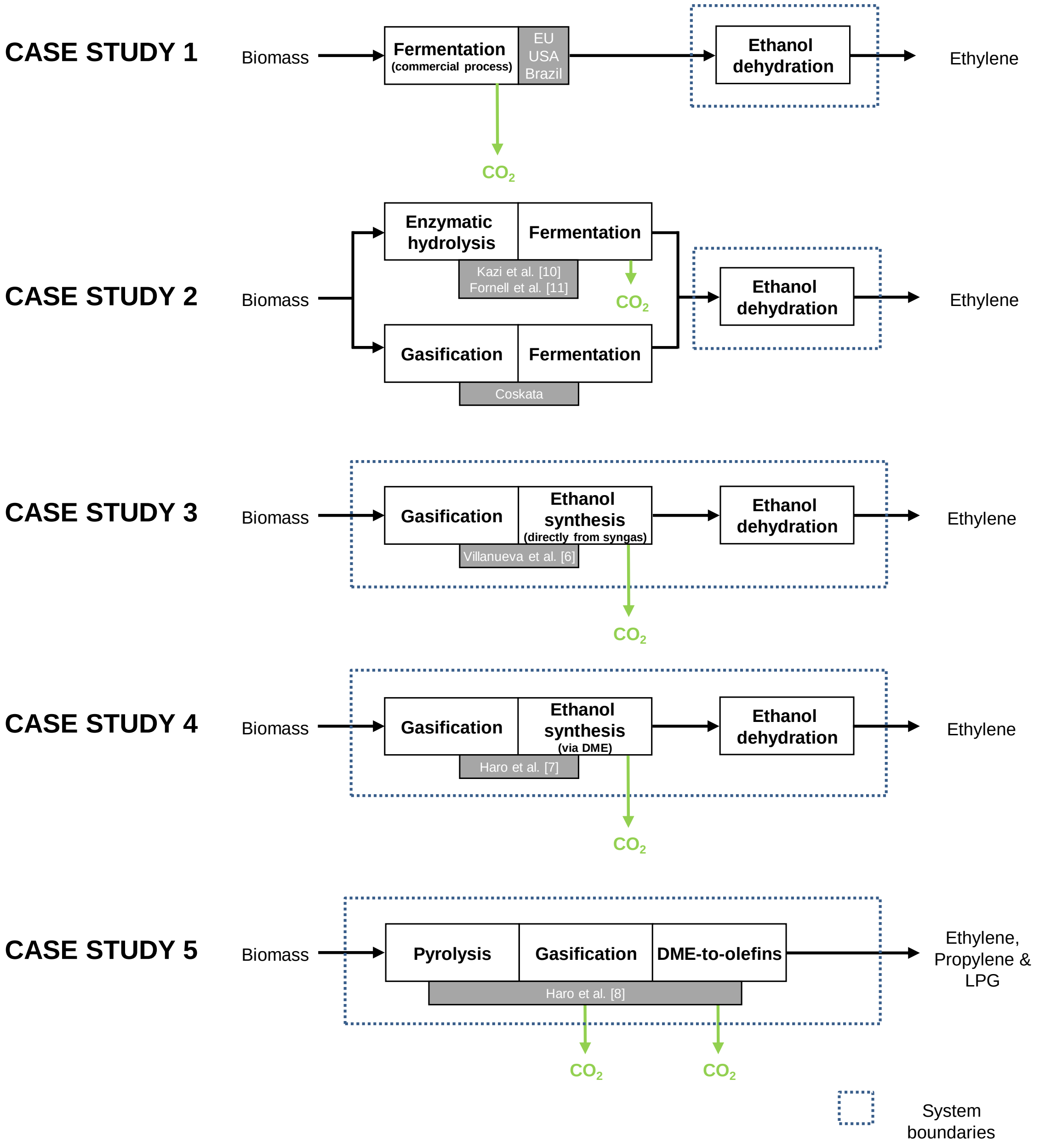

Figure 2. Outline of selected case studies and system boundaries used in this assessment.

2.1.2. Case study 2: 2nd generation ethanol via enzymatic hydrolysis and via syngas fermentation

Although 2nd generation ethanol is in an advanced stage of development, there are no commercial plants in operation, so the impact on the bioethanol commercial trading price is unknown. In this study, the only estimation of prices (production cost) has been collected from literature. Nonetheless, 2nd generation ethanol needs to be included in this assessment as it represents the most likely short-term alternative for current bioethanol production. Three alternatives are in development within 2nd generation processes: biochemical processing (via enzymatic hydrolysis), bio-thermochemical processing (via syngas fermentation) and thermochemical processing (discussed in case studies 3 and 4). Advantages and detailed discussions on current research for 2nd generation bioethanol, e.g. projects, pilot plants and techno-economic assessments, are given in [15-24]. The fermentation of biomass-derived syngas into ethanol is an extremely interesting alternative to conventional production processes and it is or has been in development by some companies, e.g. Coskata and LanzaTech. In spite of the interest in syngas fermentation, there is a lack of public information on the resulting ethanol price.

The plant size for a dehydration plant based on 2nd generation ethanol is subject to more uncertainties than in case study 1 (using current bioethanol). If a scenario of complete introduction of 2nd generation processes is selected, the ethanol production capacity of 2nd generation processes could be twice or three times greater than the largest ethanol plants (assumption by the authors). Therefore, the selected capacities in the assessment range from 300 to 1000 ML/year (236–790 tonnes/year) of ethanol.

In order to perform this technoeconomic assessment two previous assessments of 2nd generation ethanol via enzymatic hydrolysis have been selected as references, i.e. from the Chalmers University of Technology [11] and from the National Renewable Energy Laboratory (NREL) [10]. For the assessment of 2nd generation ethanol via syngas fermentation, we have assumed an ethanol price according to the latest public information from Coskata Inc. [25]. However, recent news from Coskata says that they have withdrawn their plans to use biomass and they are currently focusing on natural gas [26].

2.1.3. Case study 3: 2nd generation ethanol via thermochemical processing (direct route)

The production of bioethanol via thermochemical biomass processing involves the gasification of biomass and further conversion of syngas into ethanol. This conversion can be conducted directly, i.e. in a single catalytic reaction step, or indirectly. The direct conversion of syngas into ethanol and higher alcohols has been of great interest in the field of biomass-to-liquids (BTL) research [6, 27-35].

In this study, the technoeconomic assessment of Villanueva et al. [6] has been selected as a reference. The plant capacity is 2140 dry tonnes/day of wood chip (500 MW_{th}). The production of ethanol and higher alcohols is carried out via pyrolysis and entrained flow gasification and subsequent synthesis using a Rh- or a MoS_2-based catalyst. The bases for the conversion of syngas into ethanol and higher alcohols are summarized in Table 2. Figure 3 shows the flowchart of the process. In this study, only the alternative using MoS_2-based catalyst (a proprietary catalyst) is analyzed [6].

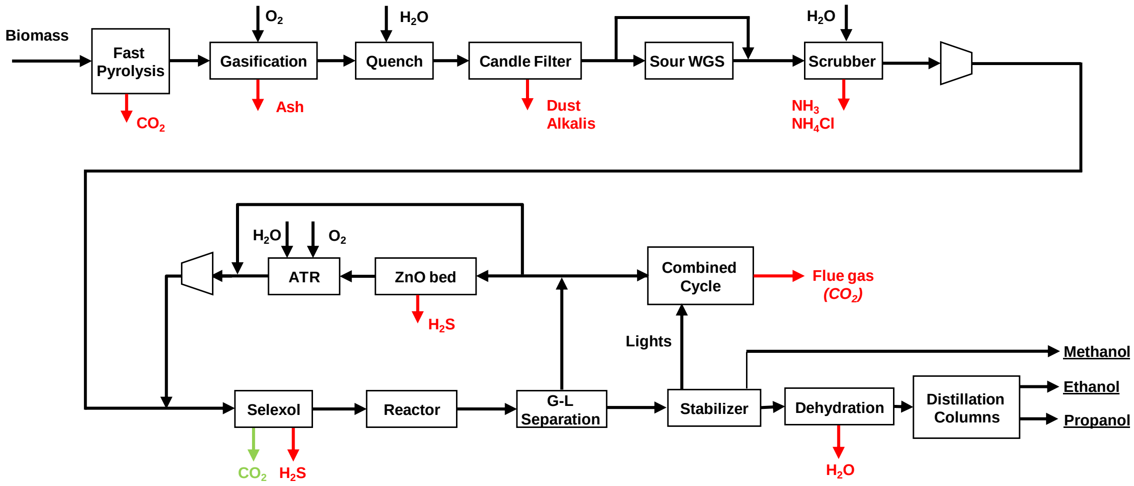

Figure 3. Process flowchart of the thermochemical production of ethanol and higher alcohols via direct synthesis (adapted from [6]).

Table 2. Process conditions for the direct synthesis of ethanol from syngas (MoS_2 Abengoa Bioenergy catalyst) [6].

Temperature (K)		573
Pressure (MPa)		9.0
CO conversion (%)		35.3
H_2/CO molar ratio		1.0
Selectivity to product (% molar)		
	Ethanol	35.4
	Methanol	7.5
	Propanol	4.2
	Light gas	17.7
	CO_2	35.2

2.1.4. Case study 4: 2nd generation ethanol via thermochemical processing (indirect route)

The direct synthesis of ethanol from syngas suffers from important limitations e.g. low selectivity, which reduces the efficiency of the ethanol production [27, 36]. Hence, the indirect synthesis via DME hydrocarbonylation has been proposed to produce ethanol from syngas with better efficiency as well as economics [7, 27, 37]. However, the indirect synthesis of ethanol from syngas is in a preliminary stage of development, therefore the DME hydrocarbonylation route is included in this study only as a potential long-term alternative.

The bases for the conversion of syngas into ethanol via DME hydrocarbonylation are summarized in Table 3 and the corresponding process flowchart is illustrated in Figure 4. In this study, only the best case of the previous assessment (i.e. CO/DME molar ratio 10:1) is included, which uses a combination of Cu-ZnO and H-Mordenite catalyst in a dual catalytic fixed-bed reactor [7].

2.1.5. Ethanol dehydration to ethylene

The dehydration of ethanol (Eq. (1)) is an established technology commercially available for the production of ethylene [2, 38-42]. In this study, the design of the dehydration process is based on commercial technology [43]. Table 4 shows the reaction conditions used for the modeling of the dehydration reactor applicable to case studies 1-4.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (1)$$

Figure 5 presents the process flowchart for the ethanol dehydration plant. The ethanol feedstock is mixed with water in a 1:1 molar ratio, pumped and preheated before entering the dehydration reactor. The outlet stream from the dehydration reactor is cooled and compressed for dewatering and conditioned for the recovery of ethylene. The gas stream requires only two fractionation columns, i.e. a first column for C_{3-} and C_{4+} hydrocarbon splitting, and a second one for the removal of ethane and propylene. The final product stream contains 99.99% (on a weight basis) ethylene with methane as the main impurity. Recovered hydrocarbons are fed to a gas combustor for thermal integration of the plant, although additional natural gas is required to satisfy the power integration of the plant.

2.2. DME-to-olefins (case study 5)

In this case study, DME instead of ethanol is used as the platform chemical for ethylene synthesis. The process has been modeled according to the bioliq® concept, which is currently being developed at the Karlsruhe Institute of Technology (KIT) and focuses on the conversion of low-grade lignocellulosic biomass, such as residual wood or straw, to synthetic fuels and other organic chemicals [44-46], as presented in Figure 6. The production of olefins (ethylene and propylene) from syngas via DME was previously modeled and assessed based on a large scale realization of the bioliq® concept in Germany [8]. Modeling of previous processing stages (i.e. pyrolysis step, production of syngas by entrained flow gasification and syngas cleaning and conditioning) are described in [47, 48].

The process conditions bases for the conversion of syngas via DME into ethylene, propylene and LPG (light gas and butenes) are summarized in Table 5 and the process flowchart is shown in Figure 7. In this study, only the best case of the previous assessment is considered [8].Compared to case studies 1-4, in this case, propylene and LPG are co-produced. The biomass input is larger than in case studies 3 and 4 (see Figure 6).

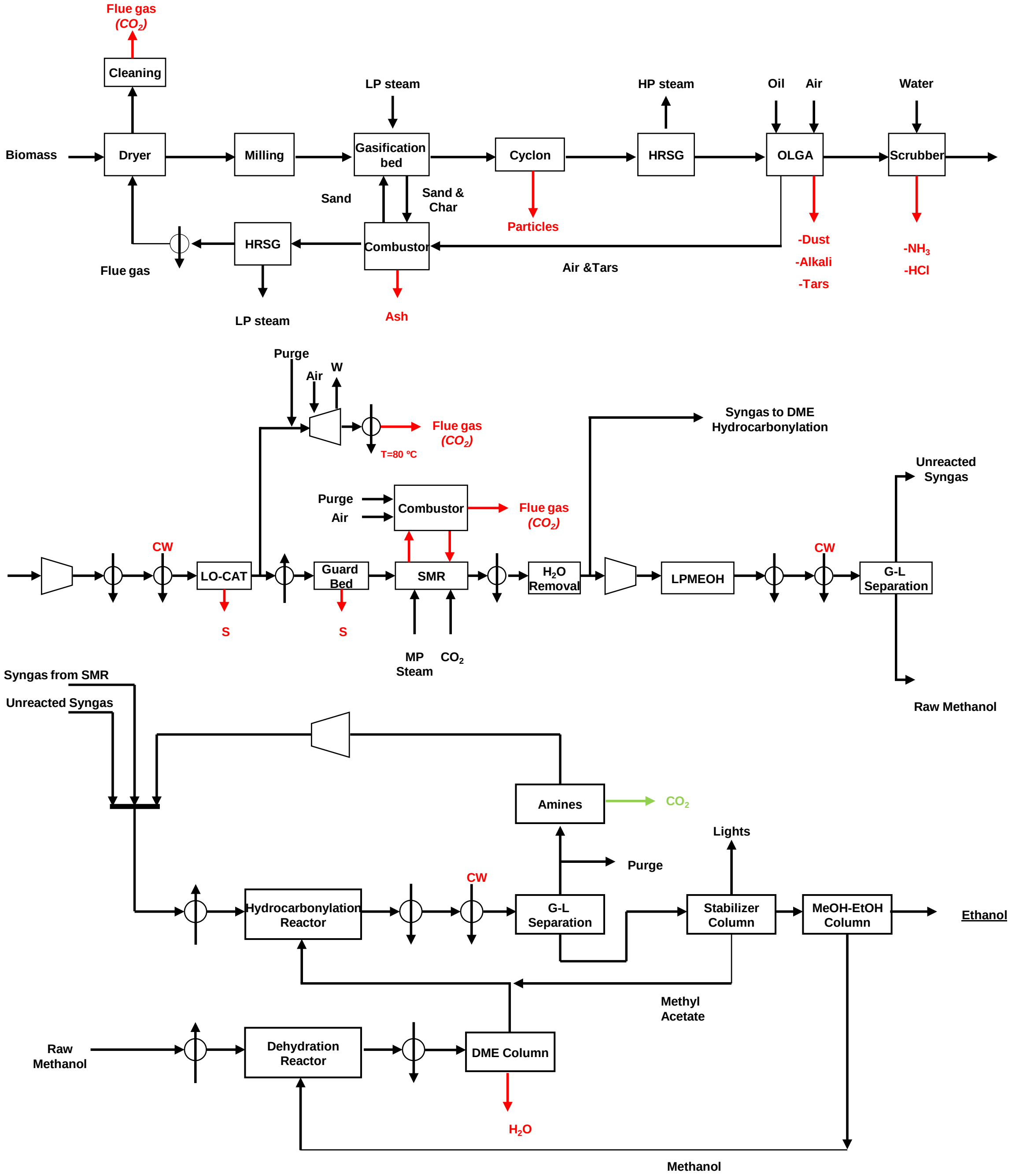

Figure 4. Process flowchart of the thermochemical production of ethanol via indirect synthesis (adapted from [7]).

Table 3. Process conditions for the indirect synthesis of ethanol from syngas via DME hydrocarbonylation [7].

Methanol synthesis	Temperature (K)		523
	Pressure (MPa)		4.9
	CO conversion (%)		31
	CO_2 conversion (%)		9
	H_2/CO molar ratio		1.70
	Selectivity to product (% molar)	Methanol	89.2
		DME	0.1
		Methane	0.1
		H_2O	10.6
DME synthesis	Temperature (K)		593
	Pressure (MPa)		2.0
	Methanol conversion (%)		85
	Selectivity to DME		1
DME hydrocarbonylation	Temperature (K)		493
	Pressure (MPa)		1.5
	H_2/CO molar ratio		1.57
	DME conversion (%)		48
	Selectivity to product (% molar)	Methanol	45.0
		Ethanol	38.0
		Methyl acetate	6.5
		CO_2	10.5

Table 4. Process conditions for the dehydration reactor (adapted from [43]).

Temperature (K)		613
Pressure (MPa)		0.48
Ethanol conversion		1
Carbon selectivity (%)	CH_4	0.10
	C_2H_4	96.50
	C_2H_6	0.50
	C_3H_6	0.05
	Butenes	2.40
	Acetaldehyde	0.20
	Coke	0.25

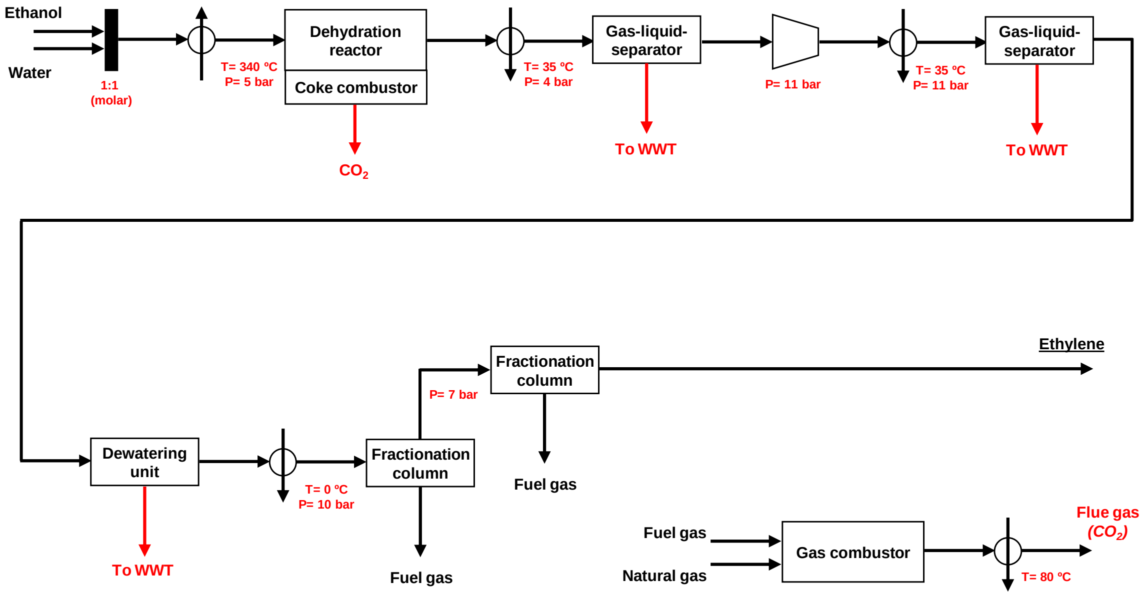

Figure 5. Process flowchart for the ethanol dehydration section.

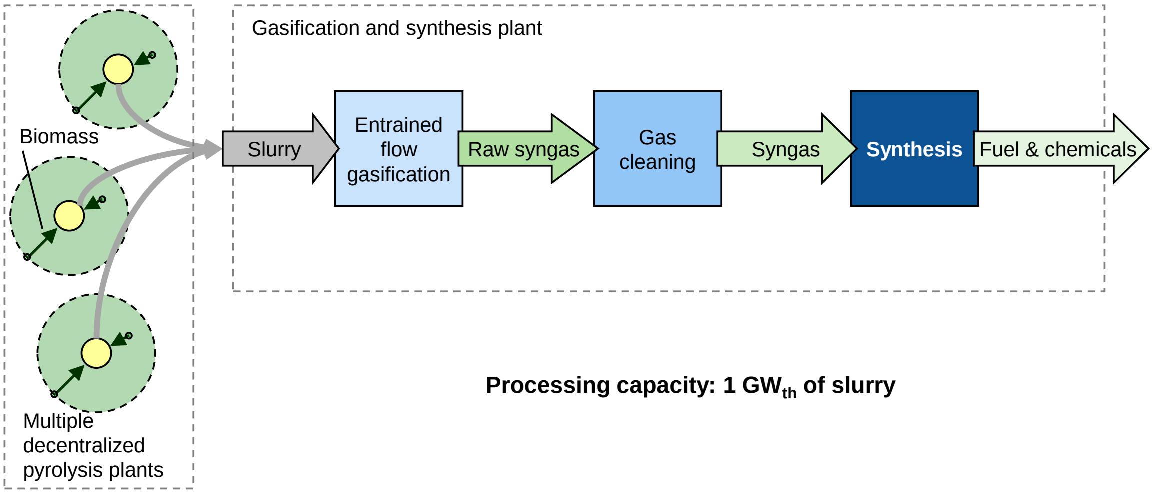

Figure 6. Overview of the bioliq® concept.

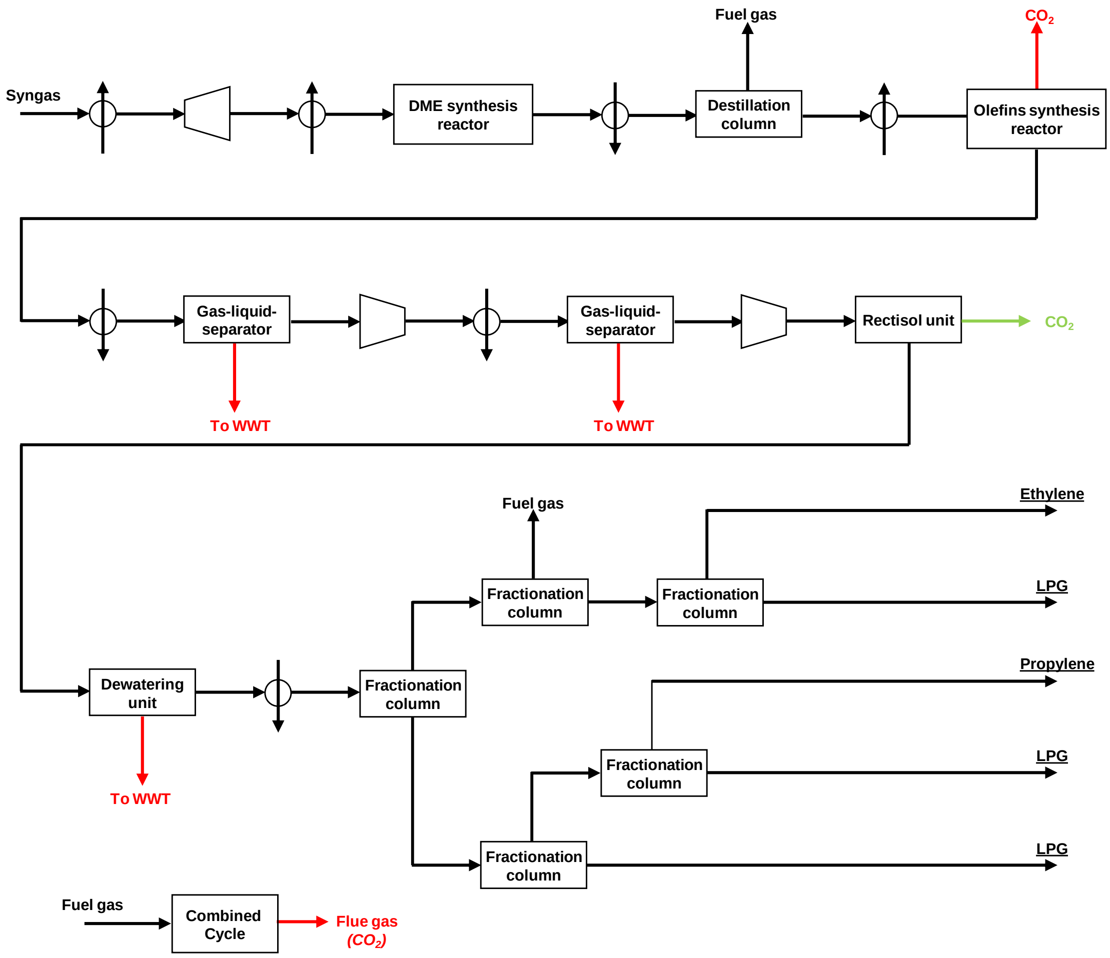

Figure 7. Process flowchart for the DME-to-olefins alternative (adapted from [8]).

Table 5. Process conditions for the ethylene production from syngas [8].

DME synthesis	Temperature (K)		523
	Pressure (MPa)		3.5
	CO conversion (%)		85
	H_2/CO molar ratio		1.0
	Product distribution (% mass)	DME	49.3
		Methanol	1.4
		CO_2	48.8
		H_2O	0.5
DME-to-olefins	Temperature (K)		996
	Pressure (MPa)		0.4
	DME conversion		1
	Inert compounds (% v/v)		39.1
	Hydrocarbon product distribution (% mass)	Ethylene	45.1
		Propylene	38.7
		Other light gases	7.9
		Butenes	8.3

3. Methodology

In order to conduct the technoeconomic assessment for the case studies, the mass and energy flows within the system boundaries are analyzed first. For this purpose, the process simulation software Aspen Plus is used. The mass and energy flow balancing builds up the foundation for the economic assessment. Fixed capital investment (FCI) estimated for the considered case studies are derived using the determined capacities. Investment dependent costs together with personnel and other operating costs, as well as revenues from by-products, lead to specific production costs for the considered products in each case

3.1. Process modeling

Below, the most important criteria and assumptions used to simulate the considered case studies are outlined. The thermodynamic methods used to model the direct and indirect production of ethanol (case studies 3 and 4) are described in [7, 6]. The dehydration of ethanol is modeled using the equation of state of Redlich—Kwong—Soave with Boston—Mathias modifications (RKS—BM) [49]. The thermodynamic methods used to model the DME-to-olefins conversion are described in [8]. The CO_2 capture, when applicable, was previously modeled in their corresponding studies ([6] for case study 3, [7] for case study 4 and [8] for case study 5).

The specific product yields of the ethanol dehydration reactor (RYield) are calculated in a spreadsheet using technical data from [43] and result in the distribution of products presented in Table 1. An analogous procedure was used to specify product yields in the DME-to-olefins reactor [8]. In case study 3, product distribution was calculated using a proprietary MoS_2 catalyst patented by Abengoa Bioenergy [6]. In case study 4, product distribution was calculated using experimental data [7].

For all case studies, rigorous fractionation columns (RadFrac) are used to give accurate results in the recovery of products and specifically for the ethylene recovery (modeled in this study). Column design and modeling in terms of molar split fractions, optimization of utility consumption and the thermal integration of columns were performed according to Smith [50] and thermal integration of the plant is described in [6, 7].

3.2. Fixed capital investment estimate

The economic assessment aims to determine ethylene production costs for the five case studies. To achieve this goal, the FCI for the ethanol dehydration, applicable in case studies 1-4, is estimated in this study (case study 5 was previously analyzed [8]). All equipment components are designed according to the mass and energy flows. As previously mentioned, in case studies 1 and 2 the FCI is calculated for a range of plant capacities, whereas in case studies 3 and 4 the FCI is calculated for a determined plant capacity. The FCI for case study 5 (DME-to-olefins) was also estimated for a specific plant capacity [8].

The investment data for the main equipment components are summarized in Table 6. The investment data for equipment components not listed in Table 6, e.g. heat exchanger and distillation columns, are calculated according to [51, 53]. The investment data are converted into €, using the yearly average exchange rate of the respective year [54], and updated to the year 2011. To account for price developments of equipment components, the price index from Kölbel/Schulze [55] is used. The presented results in section 4 for capital investment and production costs can be converted to US$ by using the average 2011 exchange rate of 1.401 US$/€.

Based on the investment data for the main equipment, the total capital investment of the ethanol dehydration plant can be estimated using ratio factors for direct and indirect capital investment according to [51], as explained in previous publications of the authors [48, 56]. Table 7 shows the assumed ratio factors for the control system, piping and further direct capital investments as well as the ratio factor for indirect capital investments, such as engineering or legal expenses. The ratio factors are selected according to process conditions, design complexity and required materials in this study. The applied ratio factor method implies uncertainties of ±30% [51].

3.3. Production cost estimate

The annual production costs consist of investment dependent, personnel and operating costs, as well as revenues from by-products (only in the DME-to-olefins case). The investment dependent costs in turn are comprised of capital costs, maintenance and tax, as well as insurance and interests on working capital. Ethanol, biomass, catalysts, cooling water and electricity make up the consumption dependent costs of each case study. The composition of the annual production costs is calculated as in [48, 56], where further information can be found. In case studies 1 and 2, the annual production cost is also evaluated for their corresponding range of plant capacities.

The personnel requirement and costs estimation are based on previous studies [44, 56, 57] based on the German workforce. Further economic assumptions used for the economic assessment of ethanol dehydration are presented in Table 8.

The production costs of ethanol in the case studies, including ethanol dehydration, have been selected subject to the origin of the ethanol. Table 9 shows the price of ethanol feedstock for each case. These production costs do not include transportation of ethanol to the dehydration plant gate.

The production cost of 2nd generation ethanol via the direct route has been evaluated in [6] and the 2nd generation ethanol via the indirect route in [7]. Both are based on biomass feedstock costs of 66 US$ per dry ton. The production cost of ethylene in the DME-to-olefin case study has been evaluated in a previous publication [8] and is based on biomass feedstock costs of 71 € per dry ton.

Table 6. Summary of investment data for main equipment components (ethanol dehydration plant).

Description	Base scale	Unit	$M€_{2011}$	Scaling factor	Reference
Dehydration reactor	2386	kmol of ethanol feed/h	2.8	0.65	[32]
Cryogenic system	13.0	MW_{th}	10.3	0.70	[51]
Compressor	1.40	MW_e	0.6	0.67	[52]
Steam generator	38	MW_{th}	6.5	0.60	[51]

Table 7. Ratio factors for direct and indirect capital investments (adapted from [51]).

Direct investments	*%*
Investment for installed equipment	100
Instrumentation and control	24
Piping	46
Electrical systems	8
Buildings	12
Yard improvements	7
Service facilities	48
Total direct investment	**245**
Indirect investments	*%*
Engineering and supervision	22
Construction expenses	28
Legal expenses	3
Contractor’s fee	15
Contingency	30
Total indirect investment	**98**
Fixed Capital Investment (FCI)	**343**

Table 8. Summary of economic assumptions.

Parameters for investment dependent costs		
Capacity factor	%	80
Expected lifetime	Years	20
Depreciation (no scrap value)	Linear	–
Interest rate	%	7.0
Working capital	% of FCI	5.0
Maintenance costs (average)	% of FCI	3.0 – 3.6
Insurance & taxes	% of FCI	2.0
Prices for consumables		
Electricity [58]	€/MWh	85.95
Natural gas [58]	€/MWh	44.50
Cooling water [32]	€/m^3	0.26
Waste water treatment [48]	€/m^3	0.32
Dehydration catalyst [32, 59]	€/kg	113

Table 9. Summary of feedstock ethanol price for case studies 1-4.

		Price	**Source**
Case study 1	Commercial price of bioethanol [a] (1st generation ethanol)	0.72 – 0.74 €/L	Europe [9]
		2.41 – 2.68 US$/gallon	USA [9]
		0.51 – 0.62 US$/L	Brazil [9]
Case study 2	2nd generation biochemical ethanol (via enzymatic hydrolysis)	0.95 US$/L	Kazi et al. [10]
		0.6 €/L	Fornell et al. [11]
	2nd generation ethanol biochemical ethanol (via syngas fermentation)	1 US$/gal	Coskata [25]
Case study 3	2nd generation ethanol via thermochemical processing (direct route)	0.710 US$/L	Villanueva et al. [6]
Case study 4	2nd generation ethanol via thermochemical processing (indirect route)	0.555 US$/L	Haro et al. [7]

[a] Data referred to September 2012.

4. Results

The following section compares the resulting mass and energy balances as well as fixed capital investment and production costs estimates for the considered case studies.

4.1. Mass and energy balances

Table 10 shows the results for the mass and energy balances for all case studies. In case studies 1 and 2, the ethanol input to the dehydration plant ranges from 150 to 500 ML/year and from 300 to 1000 ML/year respectively (see 2.1.1. and 2.1.2.). For case studies 3 and 4, the ethanol input is the value from the corresponding assessments [7, 6] and the original biomass input is also included in the system boundaries. In case study 5, all data refer to the previous publication by the authors [8], which has a fixed biomass input.

The energy efficiency to ethylene (and total products) in Table 10 is calculated according to Eq. (2), where the net input of electricity and natural gas are added when necessary. The electricity input is converted to an HHV equivalent assuming a conversion efficiency of 39%.

For case studies 1-4, in those with a dehydration plant, an additional input of both natural gas and electricity is needed. In case study 5, only electricity is imported to the plant. The energy efficiency of ethanol dehydration is quite high, so the low values of case studies 3 and 5 are due to the previous processing. Case study 4 achieves the best energy efficiency. However, the corresponding ethylene production is close to that in case study 5, in which the efficiency to ethylene halves, as a result of the different biomass input in each case study. In case study 5, the co-production of propylene and LPG enhanced the global efficiency of process as in case study 4. Case study 3 achieves the lowest efficiency despite the co-production of higher alcohols.

$$Energy\ efficiency\ (HHV) = \frac{product(s)\ (MW_{th})}{biomass\ (MW_{th}) + \frac{electricity\ consumed\ (MW_e)}{0.39} + natural\ gas\ (MW_{th})} \quad (2)$$

Table 10. Mass and energy balances for the considered case studies.

	Case study				
	1	2	3	4	5
Input to system boundaries					
Biomass in t/day (MW HHV)	N/A	N/A	2140 (500)	2140 (500)	3456 (1000)[a]
Ethanol in t/h (MW HHV)	16.9 – 53.2 (148 – 495)	33.8 – 112.6 (297 – 990)	14.5 (112)	25.9 (199)	N/A
Ethanol in ML/year	150 – 500	300 – 1000	129 [b]	230 [b]	N/A
Electricity in MW	4 – 13 [c]	8 – 26 [c]	3	6	27.0
Natural gas in MW	7 – 24 [c]	15 – 49 [c]	6	11	0
Output from system boundaries					
Ethylene in t/h (MW HHV)	9.9 – 38.9 (137 – 456)	20.5 – 68.2 (273 – 911)	8.5 (117)	15.1 (210)	16.6 (230)
Propylene in t/h (MW HHV)	N/A	N/A	N/A	N/A	14.3 (199)
LPG in t/h (MW HHV)	N/A	N/A	N/A	N/A	6.0 (84)
Energy efficiency					
From biomass to ethylene (total products) in % HHV	N/A	N/A	22.7 (30.7)	40.0	16.5 (41.1)
From ethanol to ethylene in % HHV	81.8				N/A

N/A: not applicable.

[a] Referred to bio-slurry.

[b] These values differ from references [7, 6] due to the change in the capacity factor (see Table 8).

[c] Ethanol production is not included.

4.2. Fixed capital investment

The results of the fixed capital investment (FCI) estimation corresponding to the system boundaries of this study are illustrated in Figure 8 and Figure 9. The FCI of case studies 1 and 2 is presented for both extremes of considered plant capacity (see Table 10). The FCI for case studies 3-5 is notably larger than the FCI for case studies 1 and 2, which is a consequence of the different system boundaries used in the assessment (see Figure). In order to compare the FCI, the dehydration plant of case studies 3 and 4 is also shown separately in Figure. The FCI of case study 5 is 31% and 72% larger compared to case studies 4 and 3, respectively. This difference is mainly due to the different capacities of biomass processing in these cases.

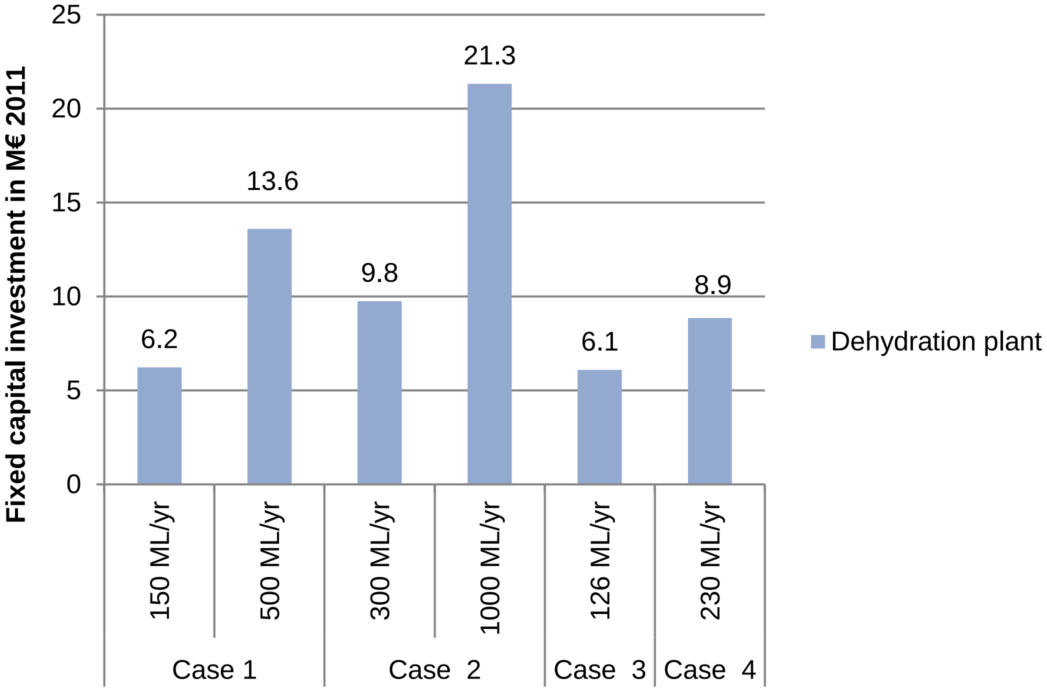

Figure 8. Fixed capital investment for the dehydration plant in case studies 1-4.

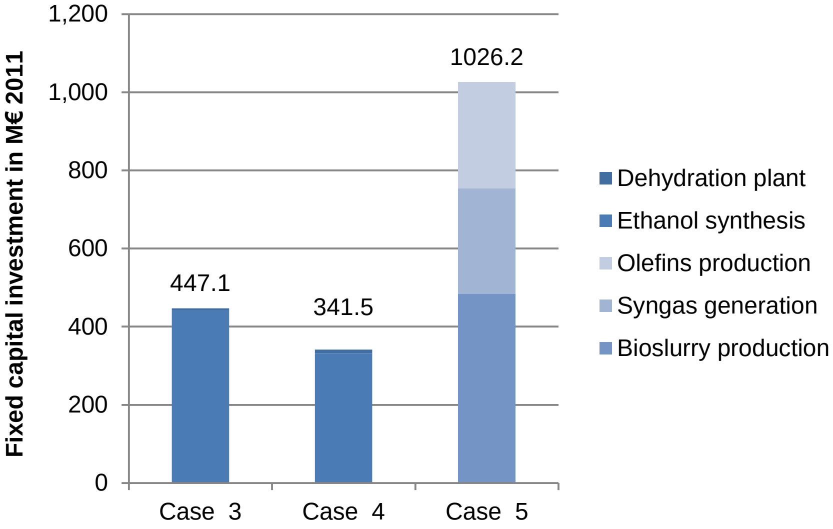

Figure 9. Fixed capital investment for case studies 3-5.

4.3. Production cost estimate

Figure 10 shows the specific production cost of ethylene for all alternatives in case study 1, i.e. using commercial prices from the EU, USA and Brazil, and for both extremes of plant capacities. Obviously, the lower the considered price of ethanol, the lower the production cost of ethylene. The contribution of ethanol cost to the total production cost of ethylene is about 91% for the lowest capacity using European ethanol and about 85% for the highest capacity using Brazilian ethanol.

Figure 11 shows the specific production cost of ethylene for all alternatives in case study 2, i.e. using estimated ethanol prices based on 2nd generation processes and for both extremes of plant capacities. As in case study 1, the price of ethanol feedstock is critical for the production costs of ethylene. For 2nd generation processes based on enzymatic hydrolysis, the production costs of ethylene ranges are about the same or slightly larger than in case study 1. However, if the considered price for ethanol via syngas fermentation were accurate, then this process could produce ethylene at a half cost compared to using commercial Brazilian ethanol.

Figure 12 shows the specific production cost of ethylene for all alternatives in case studies 3-5. The lowest value corresponds to case study 4 and the highest to case study 3. The differences between both cases are a result of the lower price of ethanol in case study 4 and the higher capacity of the dehydration plant. In case study 5, syngas, instead of ethanol, is the main contribution to the production costs of ethylene and represents 85% of the total production cost (revenues excluded).

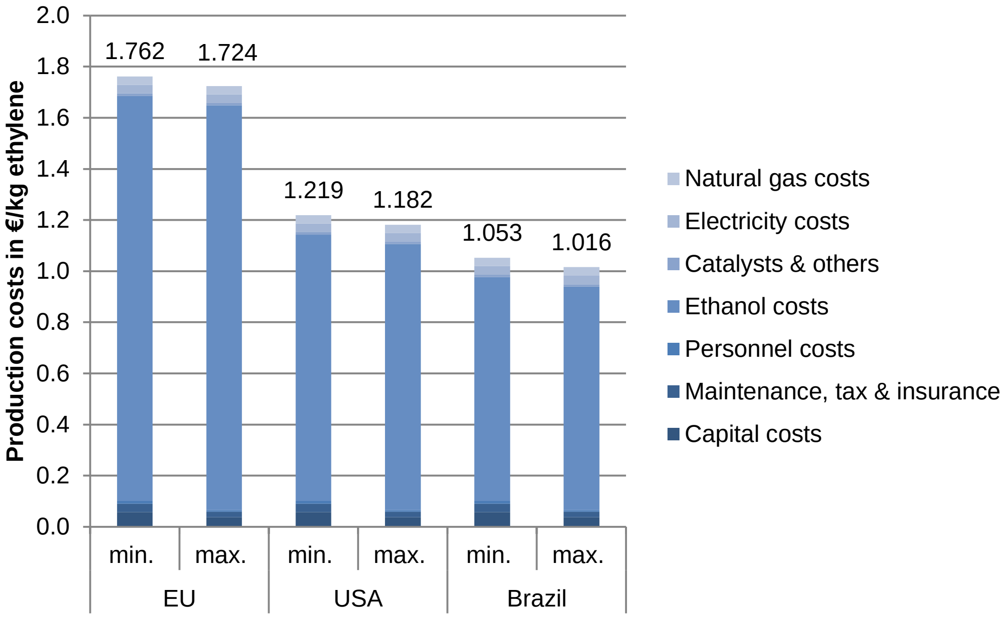

Figure 10. Specific production costs for case study 1.

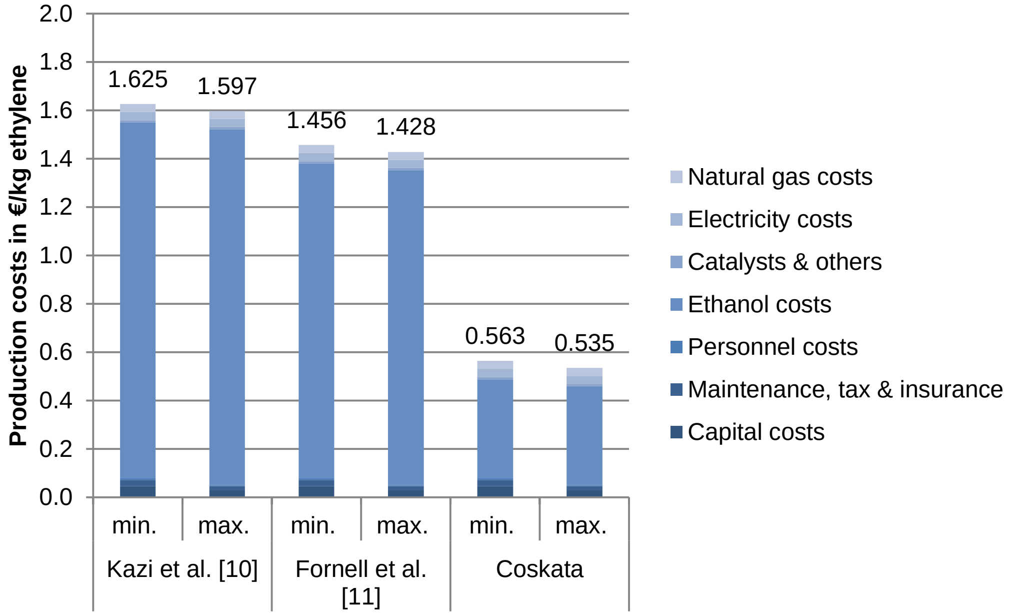

Figure 11. Specific production costs for case study 2.

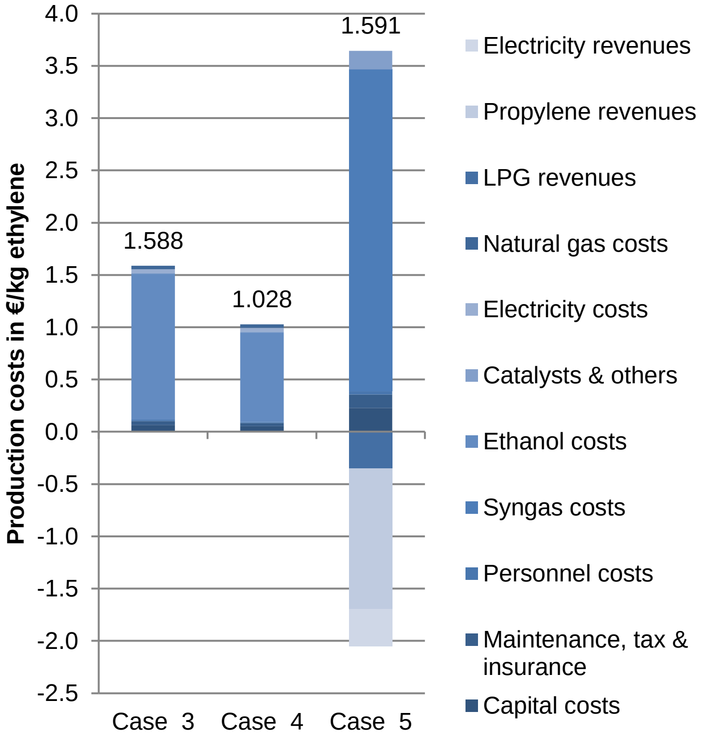

Figure 12. Specific production costs for case studies 3-5.

5. Discussion

The production of ethylene from ethanol is highly dependent on the price of ethanol feedstock (minimum 85% of production cost), which should be below 0.45 €/L in order to achieve profitability regardless of the origin of the ethanol (case studies 1-4). This ethanol price is significantly below the current price of European ethanol, similar to USA ethanol and higher than Brazilian ethanol. Nevertheless, the origin of the ethanol plays a crucial role in the future development of processes using ethanol as a platform chemical. The availability of biomass, which is actually the bottleneck for all biomass-derived products, along with the future regulation of biofuels, are the keys to the development of future bio-ethylene production. Despite the higher production cost of ethylene in case study 2 (2nd generation ethanol via enzymatic hydrolysis), the future regulations on biofuels could plunge the profit of current 1st generation ethanol by withdrawing current subsidies or limiting biomass availability. Moreover, the volatility of the ethylene price brings more uncertainty regarding the profitability of an ethanol-to-ethylene plant. For the DME-to-olefins case, the production of ethylene is not related to that of ethanol, the process is well integrated and includes the co-production of propylene and LPG. However, the uncertain availability of cheap lignocellulosic biomass and the volatility of the ethylene market price are still applicable in this case.

The production of ethylene from biomass is profitable if Brazilian ethanol is used. In the case of using ethanol via thermochemical processing (only for indirect synthesis, case study 4), the resulting ethylene production costs are also below the minimum ethylene market price in 2011 and 2012 (about 1100 €/t). However, if only the currently feasible processes for the production of ethylene from biomass are considered, the use of Brazilian ethanol would be most likely, as demonstrated by Braskem in their *green*-polyethylene plant [14]. The use of bio-ethanol for the production of chemicals reveals a controversy about the possible uses of bioethanol. Should the current use of bioethanol as a renewable fuel be diverted into the production of chemicals or should other new uses of bioethanol (as a platform chemical) be satisfied exclusively with the increase in bioethanol production? Implications of this controversy are quite serious, since the alternative uses of ethanol as a platform chemical might take over the up-to-date paradigm of bioethanol as one of the most important biofuels for the future.

5.1. Integration of ethylene production with ethanol production plants

As mentioned in section 2.1.1., the integration of ethylene production with an existent ethanol production plant has been disregarded in this study. The main reason is the economies of scale (current ethanol plants have a plant capacity of around 50 ML/year [9]). However, the integration of a dehydration plant in an ethanol production facility could benefit from important advantages if both plants are simultaneously designed and operated as a whole. Like in a dehydration plant, the ethanol stream must be diluted with water (see section 2.1.5.). If the whole production of ethanol was fed to the dehydration plant, no azeotropic distillation would be needed; which would lead to an important reduction in both investment and operating costs. The product stream from biomass fermentation would only require a soft distillation in order to enhance the concentration of ethanol up to the dehydrator requirements (see Table 4). The benefits of this integration were first commented on in the BETE (BioEthanol-To-Ethylene) process in the 1980s [12].

5.2. Integration of BECCS and comparison of the case studies

For the inventory of CO_2 emissions, only those within the system boundaries of this study are taken into account; except for case studies 1 and 2, where estimations for the synthesis of ethanol are also given. It is considered that only the CO_2 that is already captured in these cases or available at high purity will be suitable for transport and storage (marked green in Figure 3, Figure 4 and Figure 7). Hence, other sources of CO_2, like combustion gases are disregarded since they represent neither an advantage from CCS in power plants nor a benefit to the process economics. The extra energy input for CO_2 compression is assumed to come from the grid. The calculations of the CO_2 sequestration costs (comprising compression, transportation and storage) are according to the methodology described in section 3.

Table 11 shows the summary of total CO_2 emissions and integration of BECCS in the case studies. The results of the integration of BECCS are in agreement with a recent study by Meerman et al. [60], which assesses the sequestration of CO_2 in facilities using a steam methane reformer (as in case study 4), and in general with the data published by the IEA in 2011 [3], where the reduction of the capital cost for CO_2 capture (pre-combustion) is balanced with the inclusion of transportation and storage costs. The available CO_2 for storage fluctuates from about 70% of total CO_2 emissions in case study 3, where most CO_2 is captured by the Selexol unit (see Figure 3); to about 24% in case study 4, where the Amines unit is used only to remove the excess CO_2 in the ethanol synthesis loop (see Figure 4). In case study 5, there are two sources of CO_2 available for storage, both using Rectisol technology (see Figure 5). Although each case study uses a different capture technology, the CO_2 sequestration cost, i.e. the costs of capture (only compression), transportation and geological storage, are slightly different. In case study 2, considering the biochemical production of ethanol (where total emissions of CO_2 are externally given), it is possible to calculate the available CO_2 for storage (19% of total CO_2 emissions), which is much lower than in the case of thermochemical processing (case studies 3-5).

Table 11. Summary of CO_2 emissions and integration of BECCS in the case studies.

		Case study				
		1 [a] (500 ML/yr)	2 [a] (1000 ML/yr)	3	4	5
CO_2 emissions in t/h	Pyrolysis	N/A	N/A	21.9	N/A	89.9
	Gasification & conditioning	N/A	N/A	101.4	61.8	101.5
	DME-to-olefins	N/A	N/A	N/A	N/A	104.3
	Ethanol synthesis	*54.6 (only fermenter [61])*	*500.7 (total [62])*	12.1	51.2	N/A
	Ethanol dehydration (neutral CO_2)	3.7	17.5	1.0	1.7	N/A
	Ethanol dehydration (total emissions)	9.6	45.4	2.5	4.4	N/A
	Derived from the input of electricity [b]	6.5[c]	13[c]	1.5	3	13.5
	Total neutral CO_2 emissions	**58.3**	**126.8-518.2**	**136.4**	**114.7**	**295.7**
	Total CO_2 emissions	**-**	**559.1**	**139.4**	**120.4**	**309.2**
CO_2 available for sequestration in t/h	Gasification & conditioning	N/A	N/A	101.4	0	88.0
	Synthesis	*54.6*	*109.3*	0	31.3	37.4
	Total	***54.6***	***109.3***	**101.4**	**31.3**	**125.3**
Technology for CO_2 capture		N/A	N/A	Selexol	Amines	Rectisol
Extra input of electricity due to the capture in MW		*5.9*	*11.8*	10.9	3.4	13.5
Extra CO_2 emissions due to the capture in t/h [b]		*3.0*	*5.9*	5.5	1.7	6.8
Total CO_2 sequestration costs in €/t [d]		***26 [f]***		**33**	**30**	**39**

[a] In these cases the ethanol production, as well as the potential capture of CO_2 is not included in the system boundaries of this study. The given values outside system boundaries are estimated from the literature and shown in italics.

[b] Assumed to be 0.5 t of CO_2 per MWh of electricity (a typical CO_2 emission per electric MW in Europe).

[c] The production of ethanol is not included.

[d] It includes CO_2 transportation (4 €/t) and storage (14 €/t) taken from the IEA [63].

[f] A rough estimation based on [64].

5.3. Comparison of all case studies in terms of BECSS integration and plant capacity

For case studies 1 and 2, the sensitivity is represented as a function of the plant capacity, whereas for case studies 3-5 it is represented as a function of the selling price of CO_2 credits. It must be noted that the possibility of extra revenues due to CO_2 sequestration is not taken into account for case studies 1 and 2. Although the capture and storage of CO_2 in these processes seems favorable, the small capacity and the geographical dispersion of ethanol plants are the main obstacles for its implementation [61, 64]. In comparison to cases considering thermochemical processing, Lindfeldt and Westermark [65] concluded that CO_2 capture is more realizable. Currently, the main uses of CO_2 from ethanol plants are not sequestration but food processing and preservation (e.g. carbonated beverages and refrigeration), representing more than 30% of the merchant CO_2 market in USA [64].

Figure 13 shows a global outlook on the sensitivity analysis for all case studies considering BECCS. In order to compare all the case studies with each other and with the commercial price of ethylene, a transition zone (gray) has been added representing the variation of the ethylene market price from 2011 to the present along with the price of ethanol feedstock for all alternatives in case studies 1-4. For 1st generation ethanol (case study 1) the production of ethylene is profitable at current market prices, if Brazilian ethanol is used as feedstock. European ethanol should be disregarded, as it would produce ethylene at costs higher than the current commercial price. In the case of ethanol from USA, the resulting ethylene production cost would lie in the range of the ethylene market price between 2011 and 2012. The future price of 2nd generation ethanol (case study 2) is still uncertain so the curves are illustrated using dashed lines for the alternatives via enzymatic hydrolysis and a dotted line for the more uncertain case of syngas fermentation (Coskata). In comparison to case study 1, the curves decrease downwards more steadily, as a result of the higher considered capacities. Only in the case of ethanol from syngas fermentation, might the resulting ethylene be cost-competitive and it would halve the current ethylene market price. For ethanol using the thermochemical processing of biomass and direct synthesis from syngas (case study 3), the resulting ethylene price is significantly above the market price. However, assuming the possibility of selling CO_2 credits, the process would produce cost-competitive ethylene with CO_2 credits above 75 € per tonne of sequestered CO_2. In the similar case of ethanol from thermochemical processing but using indirect synthesis (case study 4), the process is profitable even without the sale of CO_2 credits. For case study 5, using thermochemical processing of biomass and syngas conversion via DME-to-olefins, the results are close to those of case study 3, except for the required CO_2 credits price. In this case, a CO_2 credit price above 150 €/t would be needed to achieve a cost-competitive production of ethylene.

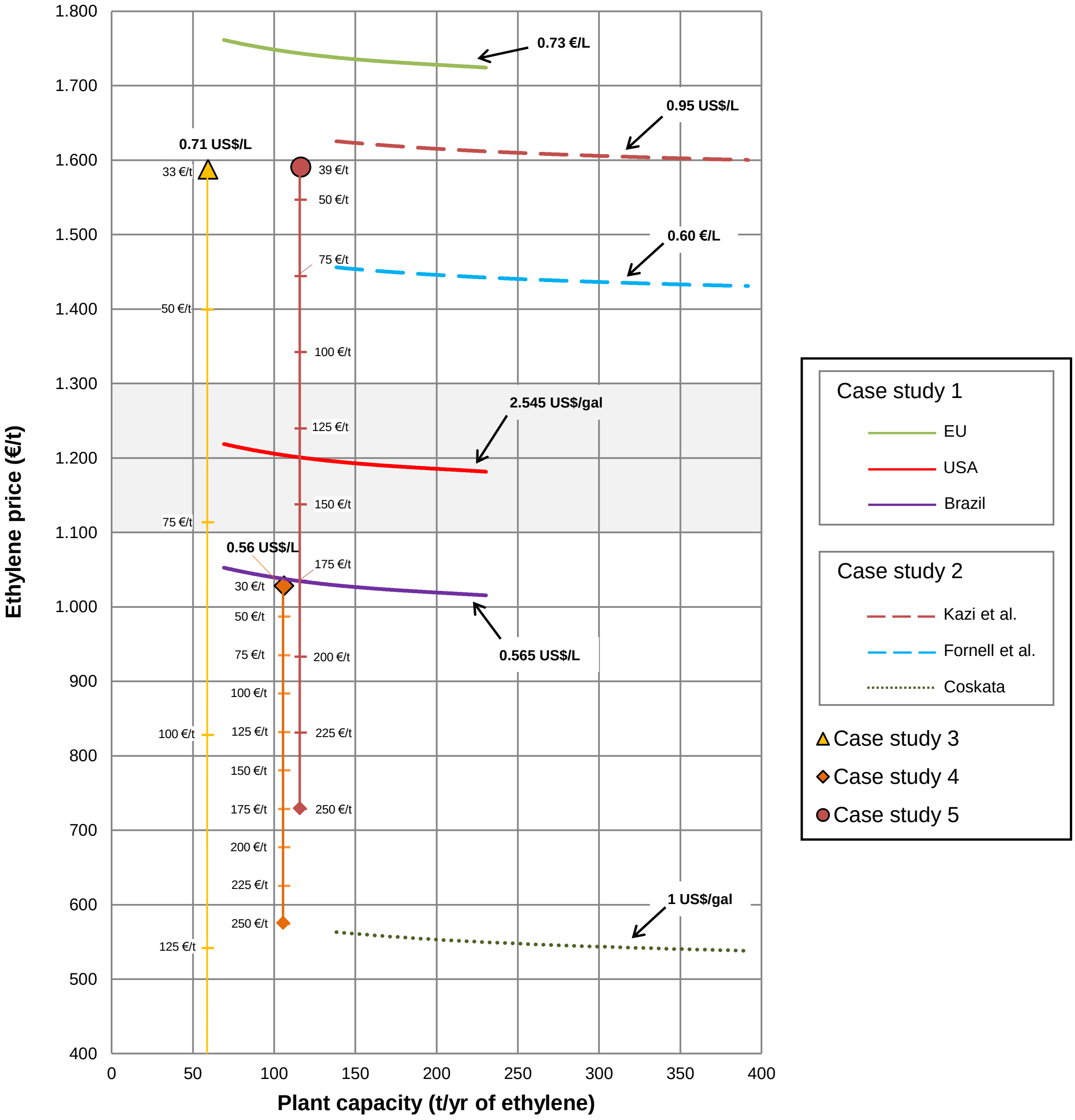

Figure 13. Sensitivity of ethylene price for the case studies as a function of plant capacity and market price of future CO_2 credits (based on sequestrated CO_2).

6. Conclusions

The presented work assesses the technical and economic viability of potential processes to produce ethylene from biomass using currently or potentially applicable technologies using technical and economic data from the bioliq® project. Two main routes are identified to this end using ethanol or DME as platform chemicals. For all case studies using ethanol, it can be concluded that the price of ethanol feedstock is crucial. Only Brazilian ethanol and the estimated price of ethanol via the indirect synthesis of syngas would enable the cost-competitive production of ethylene. However, the development of new uses for ethanol different to the biofuel application, reveals a controversy if current bioethanol should be diverted into the production of chemicals or these new uses should be satisfied only with a future increase in bioethanol production. For the case study using DME, the resulting price of ethylene is above the commercial ethylene price, but it does not require ethanol. If BECCS (Bioenergy with Carbon Capture and Storage) is taken into account for the case studies, the results would be substantially enhanced.

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Paper 4

Thermochemical Biorefineries with multiproduction using a platform chemical

This paper presents a discussion on thermochemical biorefineries focused on multiproduction using a platform chemical along with recommendations for their design and technoeconomic and environmental sustainability assessment[*].

1. Introduction

Biomass, as a wide term, represents one of the currently considered renewable energy sources for the future. Despite the novelty of the uses of biomass, this carbon-based material has been employed by mankind since the origin of time. Nowadays, biomass is still the only available feedstock for the production of some products and services, which are impossible or very unprofitable to produce using the so-called fossil fuels (coal, natural gas and crude oil). The obvious example is food, which is currently the most important use of biomass. Other examples are the manufacture of paper, the production of alcoholic drinks, cotton and other fibers and some extracts (e.g. for the pharmaceutical and cosmetic industries). The *uses* of biomass in the last century (regarding its use as a renewable energy source) were focused on the production of transport fuels, heat and electricity.

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Nomenclature

ASU: air separation unit

BECCS: bioenergy with carbon capture and storage

BTL/G: biomass-to-liquid/gas

DME: dimethyl ether

EF: entrained-flow

GHG: greenhouse gas

HHV: high heating value

IEA: International Energy Agency

LHV: low heating value

MSW: municipal solid waste

WGS: water gas shift

Biomass as a substitute of fossil feedstock for the production of transportation fuels, chemicals and materials is of great interest nowadays. Biomass is converted into products via biochemical processing (a combination of mechanical, chemical and biological technologies) and/or thermochemical processing (using pyrolysis and/or gasification technologies). The term biorefinery has been widely accepted as referring to plants processing biomass [1-9]. In the case of plants using biochemical processing, we talk about biochemical biorefineries, whereas plants using thermochemical processing would be thermochemical biorefineries. The classification of biorefineries regarding their processing could be problematic in the case of plants using both biochemical and thermochemical technologies. For example, the *two-platform* biorefinery refers to a biorefinery processing sugars via fermentation (biochemical) and gasifying the lignin to produce biofuels/chemicals (thermochemical). Another example is *bio-thermochemical* biorefinery, where the syngas from the gasification of lignocellulosic biomass (thermochemical) is fermented (biochemical).

The biochemical biorefineries are currently commercial (production of 1st generation bioethanol) since they are simple and relatively cheap plants that operate at mild conditions of pressure and temperature and due to the availability of equipment, which requires a relatively low investment. However, in thermochemical biorefineries, the operating conditions are severe for gasification, pyrolysis and synthesis, which involve a large investment cost. Hence, thermochemical biorefineries require a larger scale in order to be profitable. The required equipment for thermal processing (pyrolysis and gasification) is still not commercial. Furthermore, there are also difficulties for the cleaning and conditioning of syngas that could increase the investment cost, making the process hardly profitable. These disadvantages of thermochemical biorefineries have slowed their development along with the uncertainties in the bioenergy sector (regulation) and the volatility of the price of fossil fuels (mainly crude oil and natural gas).

In this paper, we aim to describe thermochemical biorefineries through gasification focused on multiproduction (co-production of fuels, chemicals and services), especially in the case of using a platform chemical[†]. Thermochemical biorefineries using a platform chemical are capable of producing the same products as current refineries using crude oil (not only transportation fuels, but also commodities for the chemical industry), so their products could be directly sold in current energy and chemical markets. In addition, multiproduction raises some difficulties in the assessment of sustainability and economics that requires further study.

2. Fundamentals of thermochemical biorefineries

A thermochemical biorefinery is a facility, which processes biomass by means of pyrolysis and/or gasification to produce fuels (transportation, heat/electricity generation), chemicals (high-value, commodities), materials and services (heat, electricity). In a thermochemical biorefinery, the production can be focused either on a single product, for example Fisher-Tropsch (FT) diesel, or on a mix of products (multiproduction). In a thermochemical biorefinery, biomass (syngas or bio-oil) is processed like in a petrochemical facility. For instance, the technologies and know-how from the petrochemical industry apply to the design of thermochemical biorefineries. The conversion of syngas into transportation fuels (FT-diesel, synthetic gasoline) and commodities like methanol are well-known technologies using natural gas or coal (carbochemistry) as a feedstock.

2.1. Thermochemical biorefineries focused on a single product: direct and indirect synthesis

Thermochemical biorefineries that use a direct route (syngas-to-product) for the production of a single product are known as BTL/G (biomass-to-liquid/gas) plants. In this kind of plant, the processing sections are usually easily distinguishable (see Figure 1). The design of a BTL/G plant usually suffers from a limitation of process integration and profitability, due to the maximization of the single production (e.g. larger recirculation, larger equipment, higher cost; and lower energy efficiency). The selectivity to the desired product is frequently poor in case of liquid biofuels and a large amount of subproducts (or undesired by-products) is generated in the plant. Furthermore, the operating pressure is high (e.g. 80 bar) and syngas cleaning requirements are severe.

An alternative to direct synthesis from syngas is the conversion of syngas using a platform chemical, i.e. indirect synthesis. The benefits of indirect synthesis are the overcoming of some of the technical and operational difficulties of direct synthesis, and that both net investment and operating cost are similar to in case of direct synthesis. For example, in this kind of plant, the recycling of unconverted syngas is reduced or there is not such a recycle. Since there are several (in-series) reaction steps, the syngas is fractionally converted in each reactor step and a large global conversion of the syngas is achieved without recycling. Furthermore, the milder

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[†] A platform chemical is an intermediate compound, which is further converted into a new platform chemical or into final products [10]. This definition is different to that of the IEA (International Energy Agency) used for the classification of biorefineries using four features [2].

operating pressure and optimum conversion of the syngas (in terms of required molar H_2/CO ratio) balances the inclusion of extra equipment (several reactors). An example of the benefits of this kind of plant is presented in our previous work for the indirect synthesis of ethanol using dimethyl ether (DME) [10]. The design of these biorefineries has a greater complexity and the processing sections of the plant become difficult to distinguish (see Figure 2). The use of a platform chemical involves several reaction steps, i.e. conversion of the biomass-derived syngas into the platform chemical (in 1 or 2 steps, e.g. DME synthesis), conversion of the platform chemical into the desired product, and recycle/conversion of by-products (they could be recycled to an existing reactor or converted in an on purpose reactor). Furthermore, the product separation section is larger and the process integration (material and energy) becomes crucial.

2.2. Thermochemical biorefineries focused on multiproduction: with and without the use of a platform chemical

The co-production of transportation fuels, other fuels (e.g. for heating), commodities and services (electricity and heat) creates important benefits that could be applied to thermochemical biorefineries. In a conventional (crude oil) refinery there are sorts of products which are diverted into different sectors: transport (gasoline, diesel, kerosene), petrochemical industry (olefins, BTX[‡]), and energy (LPG[§], fuel oil, electricity). Therefore, a refinery does not depend on a single market. In addition, as the refinery combines different processes, it can be well integrated energetically and materially, since all byproducts and off-gas streams are efficiently used in order to maximize the global production, i.e. enhancing energy efficiency. The benefits of co-production (multiproduction[**]) are also applicable to thermochemical biorefineries.

Multiproduction in thermochemical biorefineries could be achieved by two different approaches. One option is the combination of different direct routes (the syngas is split into different reaction steps), which would be the combination of several BTL/G processes (syngas-to-product). However, this option does not allow good integration of the synthesis areas, since, for example, the production of byproducts is not avoided. Another option is the combination of different chemical routes sharing a platform chemical (the syngas is converted into a platform chemical, which is further diverted into several reaction steps). The use of a platform chemical, such as a common intermediate, allows better material and energy integration in the plant [12]. Moreover, the platform chemical could be a product itself, i.e. not fully converted into final products. The generation of byproducts is avoided if several routes sharing the same platform chemical are used (the byproducts are diverted to other synthesis reactors, see Figure 3). In a thermochemical biorefinery with multiproduction the use of a platform chemical gives a layout similar to that in BTL/G plants, avoiding the recycling of unconverted syngas (see Figure 4).

[‡] Benzene, Toluene and Xylenes.

[§] Liquefied Petroleum Gases.

[**] In this paper, multiproduction is considered as the simultaneous co-production of products and services. A different perspective of the design of a plant producing a single product and services is given in [10].

2.3. Previous research on thermochemical biorefineries focused on multiproduction

Up to now, efforts in thermochemical biorefineries have usually been limited to BTL/G processes (single product, using a direct route). The term thermochemical biorefinery is currently scarce in the literature of the thermochemical processing of biomass [2, 4, 13-17]. Some previous assessments of thermochemical biorefineries focused on multiproduction using a platform chemical are given in [12, 17-20]. The design of thermochemical biorefineries using biomass-derived bio-oil is also scarce [22]. Regarding other kinds of biorefineries with multiproduction, examples of *two-platform* biorefineries are given in [6, 15, 23, 24]. Other studies focused on the co-feeding of fossil fuels and multiproduction combining direct routes are given in [25-29].

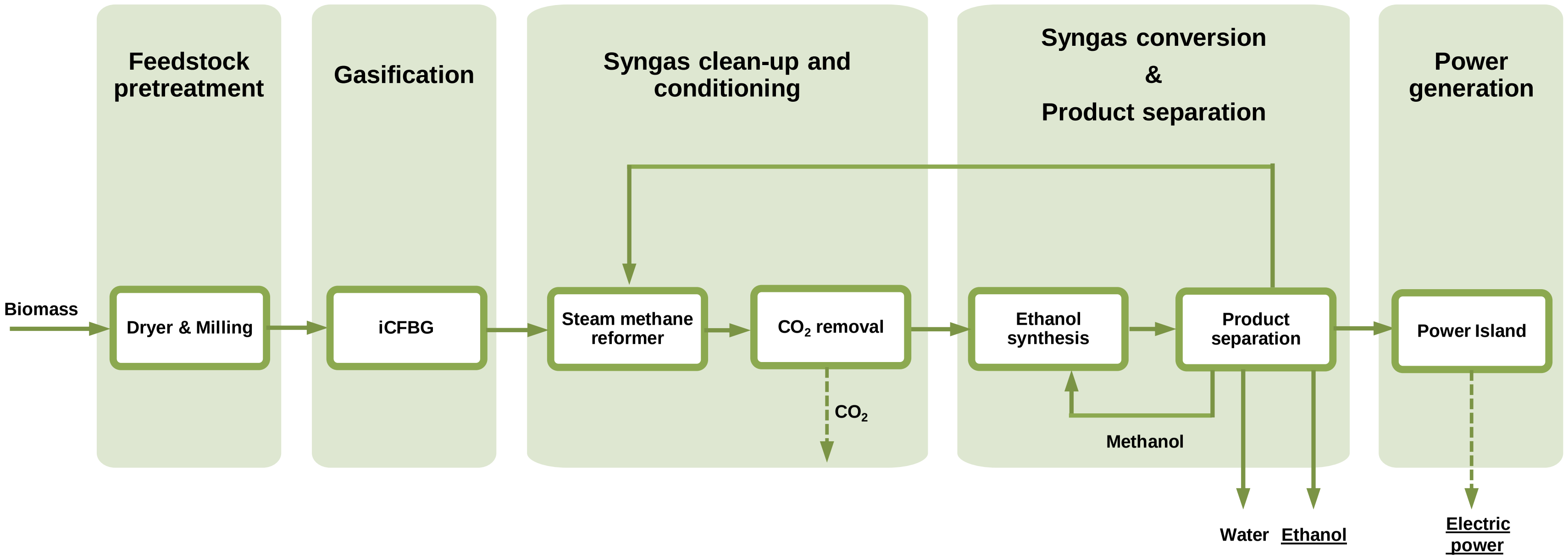

Figure 1. Scheme of a BTL/G plant (thermochemical biorefinery focused on a single product directly from syngas). Case: direct synthesis of ethanol. iCFB: indirect Circulating Fluidized Bed Gasifier.

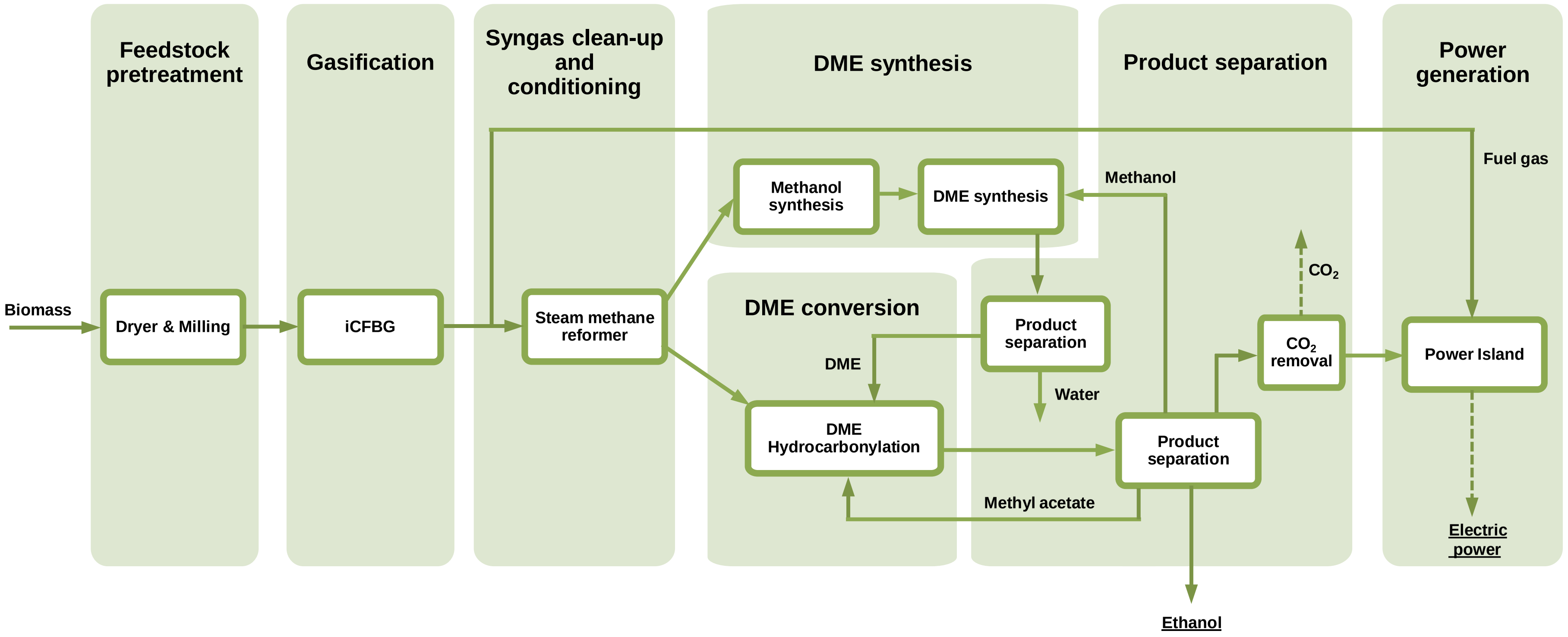

Figure 2. Scheme of a thermochemical biorefinery focused on a single product indirectly from syngas (using a platform chemical). Case: indirect synthesis of ethanol [11].

iCFB: indirect Circulating Fluidized Bed Gasifier.

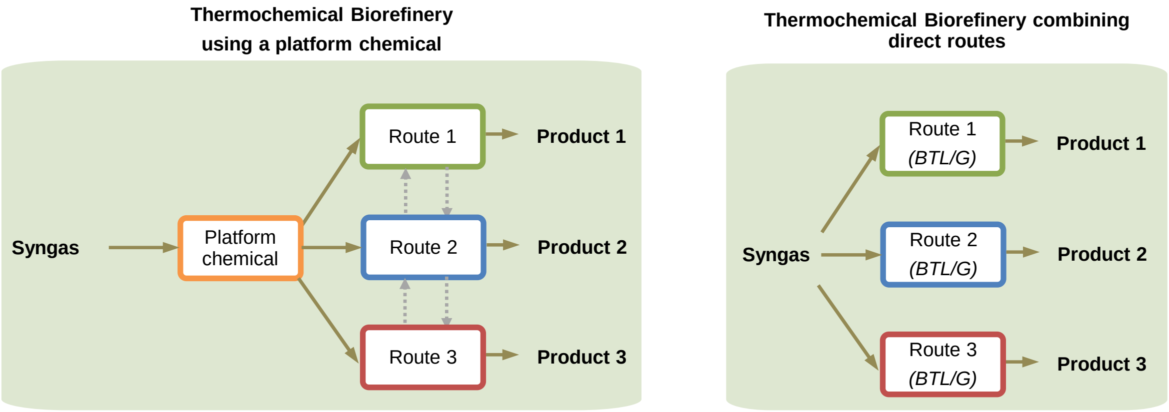

Figure 3. Different schemes for multiproduction using a platform chemical or by the combination of different direct routes from syngas.

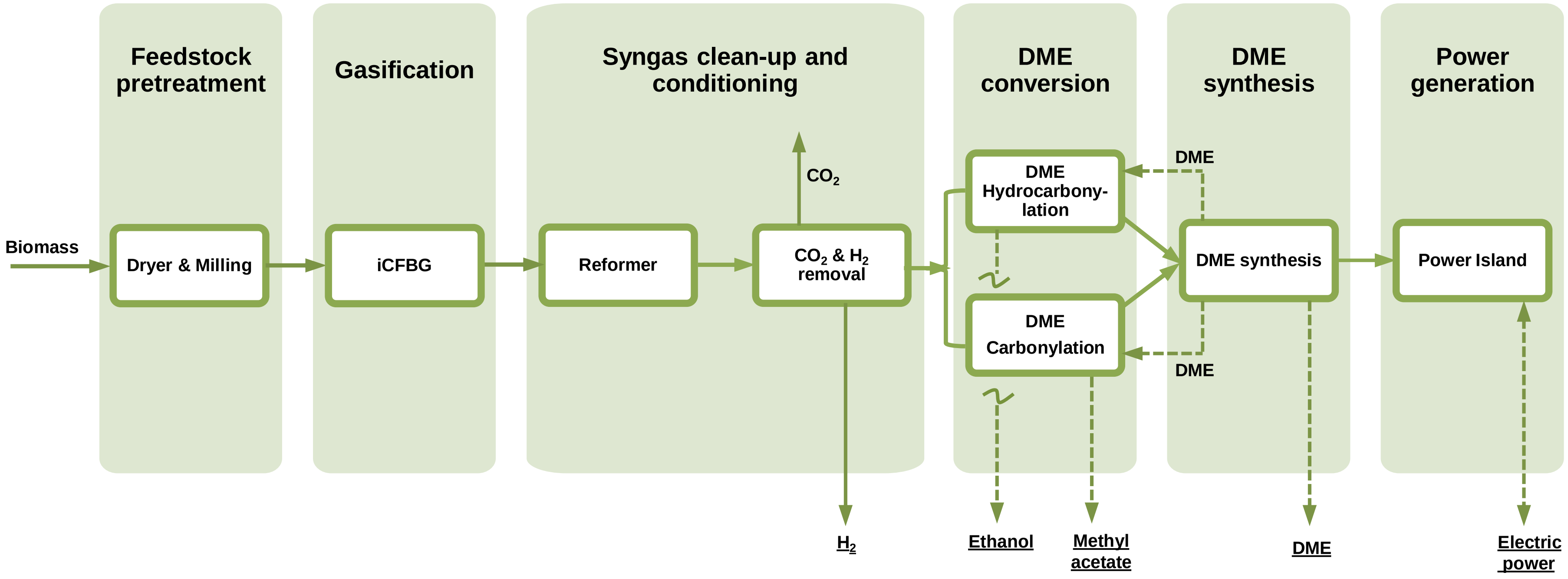

Figure 4. Scheme of a thermochemical biorefinery focused on multiproduction using a platform chemical. Case: DME (hydro)carbonylation route. iCFB: indirect Circulating Fluidized Bed Gasifier.

3. Thermochemical Biorefineries focused on multiproduction using a platform chemical

The benefits of thermochemical biorefineries using a platform chemical are:

- Better energy and material integration.
- The overcoming of some of the technical and operational difficulties of BTL/G processes (direct synthesis).
- Milder operating conditions, which balances the increase in equipment (larger synthesis and product separation areas), resulting in similar investment and operating cost as in BTL/G processes.
- The diversification of revenues, which reduces the uncertainty of the market price of bio-products.

However, this kind of biorefinery is harder to design and assess than BTL/G processes. Multiproduction involves several alternatives for the calculation of energy efficiency. The selection of the mix of products and their relative production rely on the platform chemical and the availability of chemical platform-to-products routes. On the other hand, for the economic assessment, the calculation of the minimum selling price by fixing the internal rate of return is not possible now (typical in BTL/G assessments). Alternatively, the selling price of co-products could be fixed to their current commercial value.

3.1. Energy efficiency

In a biorefinery, there are several kinds of energy qualities (products: fuels, chemicals; services: heat, electricity; and feedstock: biomass, heat, electricity). For example, the energy quality of biomass is not the same as that of electricity. The Chalmers University of Technology in its recent eBook “System perspective on Biorefineries” stated, “It is difficult to define a standard expression for evaluating efficiencies for biomass conversion processes, especially for biorefineries producing several products and energy services” [9]. This reference gives a perfect background of what this section deals with.

First, we discuss the energy qualities of the different inputs and outputs of a thermochemical biorefinery. The energy content of biomass, transportation fuels, chemicals and materials can be based on the low heating value (LHV) or the high heating value (HHV). There is some disagreement on the utilization of these energy bases in the literature, although HHV is more common. In thermochemical biorefineries, the use of a HHV basis is recommended [9]. This assumption is not so clear for the case of chemicals and materials, which are not supposed to be burned, but processed in the petrochemical industry (chemicals) or directly used (solvents, materials). However, there is not a reasonable alternative for expressing the energy content in such products.

If it is assumed that the different qualities of the products/services should be taken into account, the definition of a reference level is mandatory. The inputs to the biorefinery should be converted into their equivalent primary energy, which only in the case of the import of services (heat and/or electricity) requires the definition of conversion efficiency [9]. The definition of the system boundaries is crucial in the calculation of the energy efficiency. The task should be carried out according to the layout of the biorefinery. For example, if in the design of the process an air separation unit (ASU) has been included e.g. to supply oxygen to an EF (entrained-flow) gasifier, the energy consumption of the ASU unit must be considered in the calculations of the efficiency. In the case of importing oxygen to the biorefinery, the equivalent primary energy should be taken into account. Of course, both cases do not have to give the same result for a given design of a thermochemical biorefinery.

Table 1 shows the different definitions of efficiency used in this paper, which are in agreement with those stated by Hamelinck [30][††]. For the conversion of electricity into primary energy, a global conversion efficiency (η_e) is supposed. However, in the case of heat, despite there being a surplus in most cases, it is of low quality (low temperature) and it is wasted. Regarding the special relevance of the studies considering it in the district heating [9, 31], it is included and a global conversion efficiency (η_h) is used if necessary. The services in the biorefinery (electricity and heat) can be either an input or an output. However, they must not appear twice in the equation. For example, when calculating total efficiency, if the net electricity is an output to the biorefinery, it should be added to sum of products and not the biomass feedstock. It is also possible to use the expressions of Table 1 for the co-feeding of fossil fuels. For example, coal could be mixed with biomass for the gasification and/or natural gas reformed to produce more syngas in the plant (co-feeding) [25, 50, 51]. Of course, this extra input of energy should be accounted for in the efficiency.

In order to explain the definitions of energy efficiency in Table 1, Figure 5 shows a comparison of them for a thermochemical biorefinery using DME as a platform chemical in 12 concepts of multiproduction (see [12] for details). In the figure, the energy efficiency to all products and services ($\eta_{th,\ total}$), which is the most accurate definition in the case of multiproduction, is compared with the other definitions of energy efficiency in order to identify their weaknesses. Moreover, the possible export of heat is neglected. A first examination of the figure results in the fact that $\eta_{th,\ total}$ and $\eta_{th,\ products}$ are close (i.e. the points are close to the bisector –dashed line–) if the exported (net) electricity is small compared to the energy content of biomass feedstock. For the main product efficiency ($\eta_{th,\ main\,product}$) the values are lower than for $\eta_{th,\ total}$ (i.e. below the bisector) and the difference grows with the grade of product

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[††] In the literature, there are more examples of definitions of efficiency. Gassner et al. [31] gives an efficiency to products different to that presented here (excluding electricity from the equation) and also in terms of exergy. Furthermore, the different qualities of energy are not taken into account and e.g. electricity is not converted into equivalent thermal content.

diversification since only the main product is taken into account in $\eta_{th,\ main\,product}$. For the efficiency from syngas to products ($\eta_{th,\ products}^{syngas}$), there is a larger dependence on the electricity production/consumption in the biorefinery. In this case, the values do not lay around the bisector, but around a dotted line which represents the locus with constant biomass-to-syngas efficiency. Therefore, the different process concepts are compared without the influence of syngas production (a common step for all them). Finally, the carbon efficiency (η_C) is useful to understand how the carbon in the biomass feedstock is transformed into products (containing carbon) and gives information about how the syngas is conditioned. However, it is a misleading indicator in the case of co-producing electricity or hydrogen. For example, the lowest values of carbon efficiency corresponds to process configurations using a tar reformer, which is the technology with highest CO_2 production among those considered in the study (steam reformer, secondary reformer and tar reformer). The carbon efficiency depends on the mix of products, since in the case of co-producing ethanol, H_2 and electricity, the carbon efficiency is poor (13%), whereas the total efficiency is the greatest of the 12 concepts (51%).

Figure 6 compares the energy efficiency of different concepts of thermochemical biorefineries with and without multiproduction. First, it is important to note that the selected cases were defined (in their corresponding references) as multiproduction only when a product apart from electricity was co-produced along with the main product. In terms of $\eta_{th,\ total}^{syngas}$, the values of all cases are close (except for the co-production of ethanol and SNG where it is not available). Therefore, the inclusion of more reaction steps and a larger separation section for multiproduction does not mean lower energy efficiency. Looking at the co-production of gasoline and ethylene the resulting $\eta_{th,\ total}$ is in between the case of producing gasoline and olefins separately (plants without multiproduction), whose reaction sections are combined for the multiproduction plant. Looking at the co-production of SNG and ethanol, the resulting $\eta_{th,\ total}$ is much larger than the single production of ethanol (indirect synthesis) in a plant without multiproduction. This is because of the material integration between the ethanol synthesis and the methanation reactors (for further details see [20]). It is also remarkable the difference between the biomass-to-syngas efficiencies. Most cases have a biomass-to-syngas efficiency of 64.7% (dotted line), whereas the ethanol plant has a biomass-to-syngas efficiency of 76.6%. These differences rely on how the biomass is pretreated (e.g. pyrolysis) and the syngas produced, cleaned and conditioned. Therefore, the conversion of the syngas for both (single product and multiproduction, in terms of $\eta_{th,\ total}$,) suffers of the biomass-to-syngas efficiency. Hence, as stated in Figure 5, the comparison of thermochemical biorefineries with and without multiproduction should be in terms of $\eta_{th,\ products}^{syngas}$. Figure 6 shows that comparing the values of $\eta_{th,\ products}^{syngas}$, there is not a penalization for multiproduction in thermochemical biorefineries in terms of energy efficiency.

Table 1. Energy efficiency in thermochemical biorefineries.

Efficiency [a,b,c]	**Notes**
$\eta_{th,\ products} = \frac{products\ (MW_{th})}{biomass\ (MW_{th}) - \frac{net^{output} electricity}{\eta_e}\ (MW_{th}) - \left[\frac{net^{output} heat\ (MW_{th})}{\eta_h}\right]}$	Energy efficiency (excluding services)
$\eta_{th,\ total} = \frac{products\ (MW_{th}) + net^{output}\ electricity\ (MW_e) + [net^{output}\ heat\ (MW_{th})]}{biomass\ (MW_{th}) + \frac{net^{input}\ electricity}{\eta_e}\ (MW_{th}) + \left[\frac{net^{input}\ heat\ (MW_{th})}{\eta_h}\right]}$	Energy efficiency
$\eta_{th,\ products}^{syngas} = \frac{products\ (MW_{th})}{syngas\ (MW_{th}) - \frac{net^{output} electricity}{\eta_e}\ (MW_{th}) - \left[\frac{net^{output} heat\ (MW_{th})}{\eta_h}\right]}$	Energy efficiency from syngas [c] (excluding services)
$\eta_{th,\ total}^{syngas} = \frac{products\ (MW_{th})\ +\ net^{output} electricity\ (MW_e) + [net^{output} heat\ (MW_{th})]}{syngas\ (MW_{th})\ +\ \frac{net^{input}\ electricity}{\eta_e}\ (MW_{th}) + \left[\frac{net^{input}\ heat\ (MW_{th})}{\eta_h}\right]}$	Energy efficiency from syngas [d]
$\eta_{th,\ main\ product} = \frac{main\ product\ (MW_{th})}{biomass\ (MW_{th}) - other\ products\ (MW_{th}) - \frac{net^{output} electricity}{\eta_e}\ (MW_{th}) - \left[\frac{net^{output} heat\ (M}{\eta_h}\right.}$	Energy efficiency to the main product
$\eta_{e,\ biorefinery} = \frac{net\ electricity\ (MW_e)}{biomass\ (MW_{th}) - products\ (MW_{th}) - \left[\frac{net^{output} heat\ (MW_{th})}{\eta_h}\right]}$	Electricity efficiency in the biorefinery
$\eta_C = \frac{carbon\ in\ products\ (C)}{biomass\ (C)\ +[other\ carbon\ inputs\ (C)]}$	Carbon efficiency

[a] The terms net^{input} (consumed - produced) and net^{output} (produced - consumed) are exclusive and only the one which is positive must appear in the equation as commented in the main text. When the only option is net^{output}, it must appear regardless of the sign.

[b] If there is a positive net heat, but it cannot be used (exported), then it should not be included in the expressions.

[c] In the case of other inputs to the plant apart from biomass, e.g. co-feeding of fossil fuels, oxygen for direct gasification and/or autothermal reforming, the equivalent primary energy should be added to the denominator.

[d] In the case of the efficiency from syngas to products (and services), we consider the net electricity in the whole biorefinery, since in some configurations it is not possible to distinguish the fraction after the conditioning.

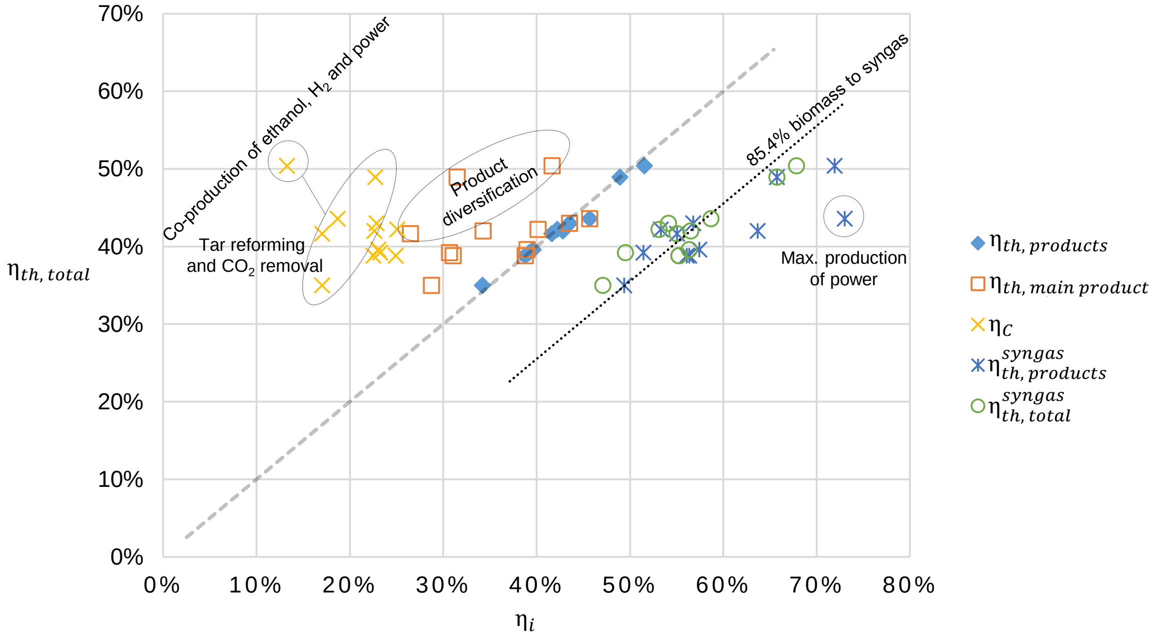

Figure 5. Efficiencies shown in Table 1 versus the total energy efficiency $\eta_{th,\ total}$ for the concepts of thermochemical biorefinery with multiproduction presented in [12] and assuming a η_e of 35%.

The dashed line (bisector) represents the values of η_i equal to $\eta_{th,\ total}$. The dotted line represents the values of η_i^{syngas} sharing the same biomass-to-syngas efficiency (same syngas production).

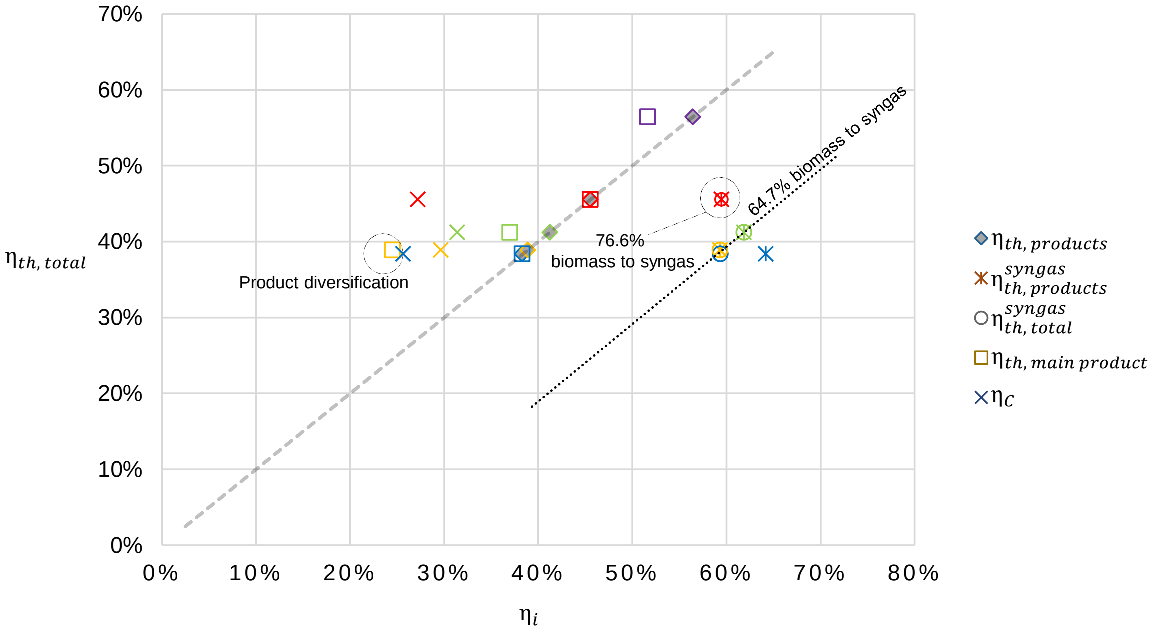

Figure 6. Comparison of energy efficiencies in thermochemical biorefinery with and without multiproduction, assuming a η_e of 35%..

w multiproduction	*w/o multiproduction*
Yellow: Co-production of gasoline & ethylene [19] Purple: Co-production of SNG and ethanol [20]	Blue: Production of synthetic gasoline [19] Green: Production of olefins [19] Red: Production of ethanol via indirect synthesis [11]

The dashed line (bisector) represents the values of η_i equal to $\eta_{th,\ total}$. The dotted line represents the values of η_i^{syngas} sharing the same biomass-to-syngas efficiency (same syngas production).

Regarding the definitions of efficiency in Table 1, the efficiency to electricity deserves further discussion. Sometimes, a neutral electric balance is imposed by producing the amount of electricity that is required in the plant. However, due to the medium to small production of electric power in the plant, the production of electricity should be carried out only using the purge and the excess heat of the plant, since the efficiency of a power plant would always be greater than the efficiency for the production of electricity in the biorefinery. Figure 7 shows the disaggregated efficiency to electricity of thermochemical biorefineries as a function of the net production of electricity. The efficiency to electricity in biorefineries is significantly lower.

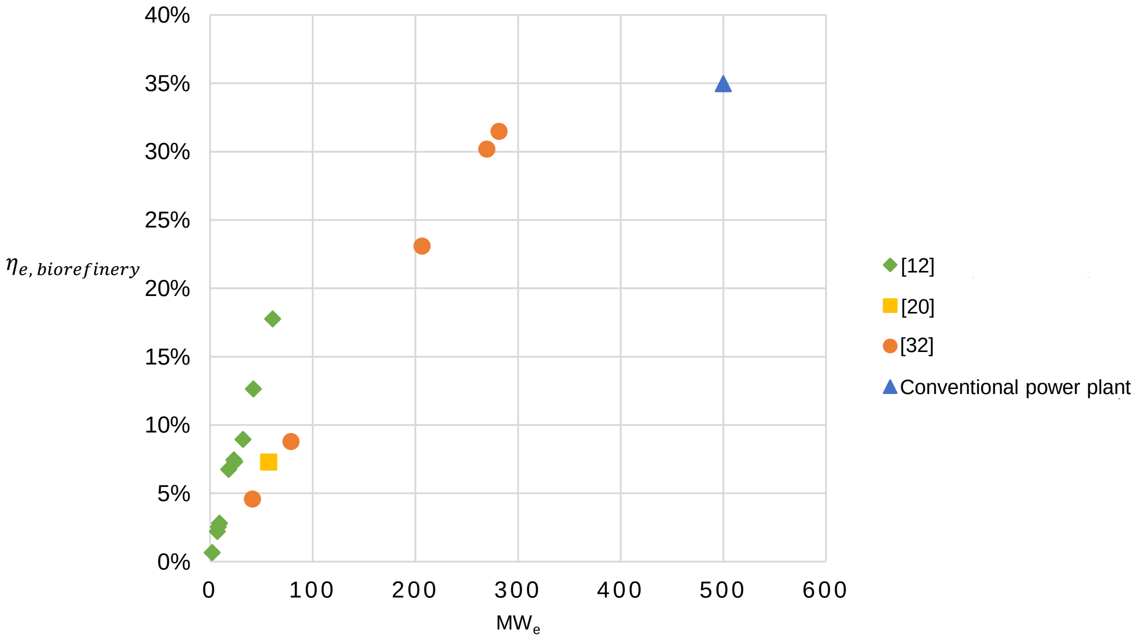

Figure 7. Efficiency to electricity for different references of thermochemical processing of biomass [12, 20, 32].

3.2. Environmental sustainability in thermochemical biorefineries

It is interesting to discuss how GHG (greenhouse gas) can be assessed in thermochemical biorefineries. According to European regulations, sustainability is achieved when there is a saving of 35% of GHG emissions compared to current transportation fuels and fuels for heat and electricity generation (60% from 2018) [33]. However, in a thermochemical biorefinery there are other products such as chemicals. The main failings and uncertainties in the assessment of sustainability in thermochemical biorefineries are:

- In the methodology given by the EU, there is no reference (emissions of the fossil reference) to the use of bio-chemicals. However, chemicals represent an important part of the global consumption of primary energy and they cannot be substituted by other renewable sources apart from biomass (the potential use of biomass in the petrochemical industry is studied in [34]). Therefore, if a global substitution of fossil fuels is an aim, bio-chemicals should be included in the assessment of sustainability.

- The allocation of co-products and services is included in European regulations but there is no explicit methodology, neither for the calculation of the GHG emissions of each co-product, nor for a medium saving of GHG emissions.
- The use of the LHV content of the co-products is mandatory in the European regulation. Nonetheless, different criteria for the allocation of products and services can be found in the literature (they are shown in Table 2, as well as their advantages and disadvantages).
- It is assumed that the final use of biofuels does not have a net impact on the global carbon balance (i.e. they are neutral). Nevertheless, the use of bio-products cannot be assumed to have a neutral emission of GHG. Of course, if the origin of the carbon in the bio-products is biogenic, the net emissions of CO_2 are zero (neutral). However, it cannot be the same with the emissions of other GHGs like VOC and NO_x. The assessment of sustainability should include the final use of all co-products and services (which is of great relevance in the case of heat, see [9]). The final use of bio-chemicals and materials is harder to account for and estimations have to be made regarding whether there is further processing (or not) and what kind of processing there might be (production of plastics, solvents, textile, etc.). Nonetheless, combustion is not one of the final uses of bio-chemicals and materials.
- In the case of bio-chemicals and bio-materials, there is net storage of the carbon of biogenic origin (they are not combusted) and it must be accounted for reducing the total emissions per MJ of product and year. However, European regulations do not consider it. Of course, this storage is not permanent although neither is the storage in biomass. In a first approximation, the retention of the carbon content in bio-chemicals and materials could be estimated by an emission factor (% of equivalent CO_2 in the bio-chemical).
- The definition of the reference system (conventional process: using fossil fuels) is hard to carry out in thermochemical biorefineries. However, the ISO 14064 states that such a definition of the conventional process is crucial [35]. For example, in the case of bio-chemical production, [36, 37] analyzed the GHG emissions of several bio-chemicals and compared them with the equivalent fossil process. However, it is difficult to determine the emissions of chemicals and materials as there is a multitude of fossil processes and public information is scarce.
- Indirect land-use change is under discussion and it is not yet regulated in the EU. The application in thermochemical biorefineries depends on the feedstock, and contrary to 1st generation processes there is a wide diversity of potential feedstocks for thermochemical biorefineries (lignocellulosic biomass, agricultural and industrial residues, MSW: municipal solid waste, etc.).
- A parallel question is the cost of opportunity of the biomass and residues and the different uses that they could have (similar to indirect land-use change). For example, the use of residues is assumed to account for zero emissions according to European regulations, but it is not true that the use of residues involves neutral GHG emissions. In the case of MSW, the deposition in landfills generates methane and VOC that will be emitted into the atmosphere (in the case of efficient landfill administration, the emissions are lower and the

case should be further studied). Therefore, as commented in [9], there would be a reduction of GHG emissions.

- In the assessment of sustainability in biorefineries, the resulting saving of GHG emissions could result in the net emissions of the process (cradle to grave) being lower than the maximum allowed in order to achieve sustainability. In this case, an extra saving is achieved [38]. This extra saving represents an opportunity for the enhancement of the profitability of such plants if a translation into an economic parameter is possible. One option is to transform the extra saving of the biorefinery into extra-avoided emissions[‡‡]. The sale of these extra-avoided emissions would enhance the profitability of the plant. Another option is to consider the co-feeding of coal and/or natural gas to reach the limit of GHG emissions in order to achieve sustainability.
- The incorporation of BECCS (BioEnergy with Carbon Capture and Storage) to thermochemical biorefineries may be a quite interesting option for the profitability of biorefineries[§§]. However, the sequestered CO_2, i.e. an outlet of CO_2 from the atmosphere, does not necessarily imply that they are extra-avoided emissions. For example (see Figure 8), in a thermochemical biorefinery with BECCS, the assessment of sustainability could give different cases (under the framework of European regulation):
    A. The process before BECCS incorporation achieves a lower saving in GHG emissions than that required by the regulation. The incorporation of BECCS allows the biorefinery to just achieve the regulation. In this case, the sequestrated CO_2 cannot be considered as negative emissions that could be economically valorized.
    B. The process before BECCS incorporation achieves a lower saving in GHG emissions and the incorporation of BECCS allows the biorefinery to achieve a saving larger than that regulated. In this case, the sequestrated CO_2 cannot be completely counted as negative emissions that could be economically valorized. Only the fraction of CO_2 that is an extra saving with respect to the regulation could be valorized (extra-avoided emissions).
    C. The process before BECCS incorporation achieves the same saving in GHG emissions as that required by the regulation. In this case, the sequestrated CO_2 counts as negative emissions that could be economically valorized.
    D. The process before BECCS incorporation achieves a larger saving in GHG emissions than that required by the regulation. In this case, there is an extra saving that does not depends on the sequestrated CO_2, which again counts as negative

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[‡‡] Extra-avoided emissions are cited here as the amount of equivalent CO_2 that is avoided (not emitted to the atmosphere) above the regulation requirements of sustainability. If a thermochemical biorefinery achieves a larger saving than the required, then the extra saving could be translated into extra-avoided emissions (e.g. t/h of CO_2).

[§§] The capture of CO_2 in a thermochemical biorefinery is favored, since it would be in pre-combustion reducing the cost of the capture compared to conventional power plants [19].It is recommended by the IEA as a potential way to improve the reduction of carbon emissions to the atmosphere. A further reading of CCS incorporation in facilities using fossil fuels is given in [39].

emissions that could be economically valorized. Hence, it would be possible to sell a larger amount of CO_2 credits than those from BECCS incorporation (negative emissions). If it were not possible, the whole extra-avoided emissions would not be valorized, penalizing the thermochemical biorefinery.

Table 2. Alternative for the allocation of GHG emissions in biorefineries.

Allocation		**Advantages**	**Disadvantages**
Mass	C content	It focuses on the main sources of GHG emissions.	It disregards the production of non-containing carbon products (e.g. H_2) and all services.
	Total mass	It takes all products into account.	Services are disregarded. There is not a direct relation between mass content and energy efficiency.
Energy	HHV basis	It takes into account all products and services. It gives a clear indication of the efficiency of the process.	It considers equivalent chemicals and materials to fuels.
	LHV basis	It takes into account all products and services. It is the regulated allocation in the EU.	It considers equivalent chemicals and materials to fuels.
Economic value	Present prices (of the functional unit)	It gives an accurate view of the potential of GHG reduction in currently demanded products and services.	It could be inaccurate for bio-products whose present prices are only an estimation of their potential market.
	Future/expected prices (of the functional unit)	It shows the potential of GHG reductions in estimated economic scenarios, e.g. in a bio-based economy with high competition within biorefineries.	It is based on an estimation of the future behavior of the market.
[Regulations]	EU (energy basis: LHV) [33]	It is the legal way in the EU for the certification of biofuels.	It does not consider the final use of bio-products. It is not true that the production of electricity from biomass is a carbon neutral activity when using residues.
	ISO 14044 (no allocation) [40]	It is the way for international certification of bioproducts.	It forces the selection of the final use of all products and services, which may be unaffordable in the case of chemicals and materials.

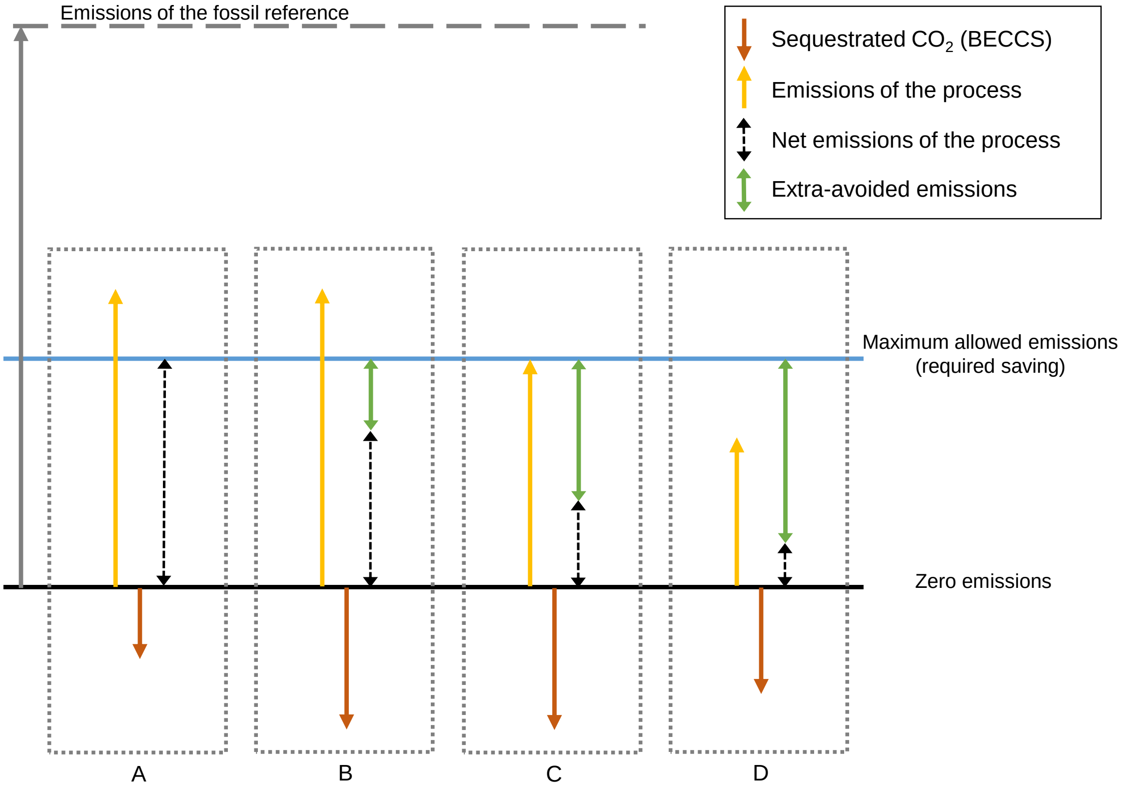

Figure 8. Different cases when BECCS is incorporated into thermochemical biorefineries.

A proposal of methodology for the assessment of sustainability in thermochemical biorefineries with multiproduction is shown in Paper 7 [38], where the commented upon failings are further discussed.

3.3. Process design

The design of thermochemical biorefineries with multiproduction is a hard task. The use of general guides for thermochemical processing [31, 41, 42] is helpful. However, regarding the peculiarities of these kind of biorefineries, the design of a thermochemical biorefinery requires of the combination of a large number of technical (gasification, cleaning, conditioning, synthesis) and economic (mix of products, regulation of the sector, investment) considerations. Some of them are common in the design of conventional BTL/G processes, but others are inherent to multiproduction and the use of a platform chemical.

In a thermochemical biorefinery with multiproduction, at least a fuel (low-value high-volume) and a chemical (high-value low-volume) should be co-produced in order to achieve maximum profitability. In this case, the benefits of a large-scale facility can apply to the production of low-volume products, and the income from their sale will contribute to making a plant profitable, which otherwise would produce only low-value high-volume products[***]. Hence, the first step is to define, according to the selected economic scenario, which fuel(s) and chemical(s) will be

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[***] This idea is commonly misleading in the literature of biomass valorization. A study on the matter can be found in [43].

produced in the plant, i.e. the mix of products. According to the selected mix, a platform chemical and the corresponding chemical routes (platform-to-products) are selected. Thereafter, the gasification, cleaning and conditioning technologies can be defined. For the gasifier, the typical parameters for the design/selection are the required pretreatment, the gasifying agents (e.g. O_2, which would require an ASU plant), the operating pressure, and the requirements of further cleaning, the yield of light hydrocarbons and the resulting molar H_2/CO ratio. For plants with multiproduction, only the H_2/CO ratio requires further discussion with respect to conventional BTL/G plants. Moreover, in multiproduction plants using a platform chemical, the integration of reaction steps (material and energy) is also more complex than in BTL/G plants. Hence, a discussion on energy and material integration is appealing.

A comprehensive study of all aspects of the design of multiproduction plants is beyond the scope of this paper. Nonetheless, in order to give a fair discussion of the design of thermochemical biorefineries with multiproduction, a set of different case studies is presented using DME as the platform chemical. These case studies are simplifications limited to the main aspects that differentiate thermochemical biorefineries with multiproduction using a platform chemical.

3.3.1. Case studies using DME as platform chemical

The potential products using DME as the platform chemical are shown in Table 3, whose combination gives the mix of products of the biorefinery. In the case of the services, the net export/import will be determined after the design and by calculation of the material and energy balances (technical assessment). Also in Table 3, the conversion routes for the production of each co-product are shown along with their final use. The required H_2/CO ratio for the synthesis of each individual product depends on how DME is synthesized from syngas.

Case study 1: material integration in a plant producing DME and ethanol

- It is important to achieve high efficiency (e.g. achieving an efficient conversion of syngas), but not to increase the complexity (related to the fixed capital investment) of the plant too much. In the DME hydrocarbonylation route, methanol is also produced along with ethanol (in a molar ratio 1:1). However, the generated methanol could be dehydrated into more DME via dehydration [21]. The conversion of the methanol does not require a new reactor; it can be done in the DME synthesis reactor [12, 11], so there is not an increase in equipment in the biorefinery. Therefore, the material integration of the biorefinery allows that the by-product (methanol) is completely converted in the plant producing more DME and ethanol.

Table 3. Potential products using DME as platform chemical.

Product [a]	**Use**	**Route**	**H_2/CO ratio** [b]	
DME	*Fuel/Chemical*	-	*1* *(one step)*	*2* *(two steps)*
Ethanol	Fuel/Chemical	DME hydrocarbonylation	2/3	2
Methanol	Fuel/Chemical	DME hydrocarbonylation	5/4	-
Methyl acetate	Chemical	DME carbonylation	3/4	4/3
Acetic anhydride	Chemical	Methyl acetate carbonylation	3/5	1
Ethylene	Chemical	DME-to-olefins	1	2
Propylene	Chemical	DME-to-olefins	1	2
LPG	Fuel	DME-to-olefins and DME-to-gasoline	1	2
Synthetic gasoline	Fuel	DME-to-gasoline	1	2
Diesel	Fuel	DME-to-fuels	1	2
Jet fuel	Fuel	DME-to-fuels	1	2

[a] Prior to the generation of DME, H_2 and CO_2 could be separated (conditioning of the syngas) and can join the mix of products. Furthermore, in the synthesis and conversion of DME, CO_2 is commonly a by-product of the reactions (incorporation of BECCS). The DME itself can be a product of the biorefinery.

[b] The H_2/CO ratio is required depending on how the DME is synthesized from syngas. For further details, see [10].

Case study 2: selection of the mix of products if an EF gasifier is introduced

- If a gasifier producing a raw syngas with a low H_2/CO ratio (0.5) and without tars is considered for the gasification of biomass, then DME will be more efficiently synthesized from syngas in a single reaction step (ratio of 1). The potential products should also be limited to those that require of a low H_2/CO ratio. For example, a candidate mix of products could be DME (fuel substitute for diesel and/or natural gas), methyl acetate and acetic anhydride (high-value chemicals). The average H_2/CO ratio of the mix ranges from 1 to 3/5 (varying as a function of the relative volume of production of each co-product). The raw syngas from the gasifier, which does not require special conditioning (cleaning) for synthesis, must in this case, be conditioned by means of WGS[†††] to slightly increase its H_2/CO ratio. The selection of a mix of products with higher hydrogen requirements (higher H_2/CO ratio), would result in a need for larger equipment for syngas conditioning (higher investment and operating costs) and lower energy and carbon efficiency (less revenues and worse carbon conversion).

[†††] The WGS (water gas shift) reactor involves a loss of chemical energy and a loss of carbon in the plant.

Case study 3: selection of mix of products using an i-CFB (indirectly-heated circulating fluidized bed) gasifier and a tar reformer

– If a gasifier with a high production of tar and light hydrocarbons is considered for the gasification of biomass, the removal or conversion of tars is mandatory prior to the conversion of the syngas. A tar reformer converts the tars and light hydrocarbons into more syngas, achieving a H_2/CO ratio of around 1.5. The considered products are DME, ethanol (substitute for gasoline and chemical) and olefins (precursor of plastics). In this case, DME is more efficiently synthesized in a single step.

Case study 4: process integration

– In the integration of the process, it is of interest that the conversion of the syngas in each reaction step is carried out when it has the optimal H_2/CO ratio. For example, consider a plant with an i-CFB gasifier and a tar reformer aiming to produce DME and methyl acetate (as in case study 2). The raw syngas in the biorefinery has a H_2/CO ratio of 1.5, which is larger than the average required in the conversion into products (around 0.8). Hence, hydrogen can be separated, and the recovered hydrogen sold as a co-product (low-volume). In this case, the layout brings an advantage for the recovery of hydrogen. Contrary to a plant focused on the production of hydrogen (single product), in the considered biorefinery the maximum production of hydrogen is not sought. Therefore, the production of hydrogen requires lower investment and operating costs (there is not a combination of low and high temperature WGS reactors) than in plants producing hydrogen as single product. Regarding the process flowchart (Figure 9), the fresh syngas is not used for the synthesis of DME, but for the carbonylation of DME. Examining the reaction conditions of the DME carbonylation, the reaction requires a large excess of CO with respect to the stoichiometry CO/DME molar ratio. The presence of hydrogen does not penalize the reaction [12]. Therefore, the syngas is efficiently converted in the biorefinery.

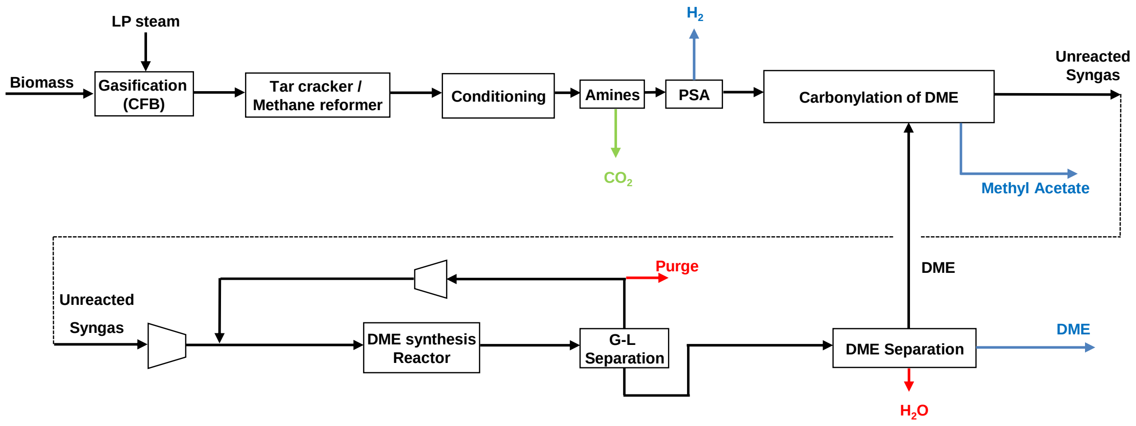

Figure 9. Process flowchart of a thermochemical biorefinery co-producing DME, methyl acetate and hydrogen (adapted from [12]: TR-05 concept).

iCFB: indirect Circulating Fluidized Bed Gasifier. PSA: Pressure Swing Adsorption.

3.4. Economic assessment

In the economic assessment of new plants, such as thermochemical biorefineries with multiproduction, there are important uncertainties that make the resulting profitability unclear. Examples of such uncertainties are the cost of the processing technologies (gasification, syngas cleaning), the price of biomass (feedstock) and the evolution of the bio-products market (prices) and their regulation. The case of thermochemical biorefineries is somehow easier than biochemical biorefineries, since the potential bio-products are those currently used or proven substitutes for the fossil equivalents. Nonetheless, the profitability of thermochemical biorefineries requires, due to the larger scale of the plant, a larger investment

For the economic assessment of thermochemical biorefineries with multiproduction, the presence of more than one main product forces an alternative to the calculation of the minimum selling price (once the internal rate of return is fixed). The problem relies on multiproduction, which gives as many variables for economic assessment as co-products the plant has. In order to address the problem, there are two options, although neither is as illustrative as the minimum selling price:

- The commercial price of co-products and services are fixed. In this case, the internal rate of return (IRR) is the result of the economic assessment.
- The IRR is fixed. In this case, the % of change over the market prices of co-products and services is calculated (the % of change is common for all products).

An example of an economic assessment by fixing the commercial price of products is given in [12], where the resulting IRR were highly satisfactory when a bio-chemical (methyl acetate) is co-produced along with a biofuel (DME). The calculation of the % of change was carried out in [19], where the case of multiproduction (production of gasoline and ethylene) achieved profitability between the cases of single production of a fuel (gasoline) or a chemical (olefins), despite the greater complexity of the plant.

4. Conclusions

The inclusion of multiproduction in thermochemical biorefineries using a platform chemical is discussed and analyzed in this paper. Multiproduction in thermochemical biorefineries allows the co-production of different sorts of products: transportation fuels, fuels for heating, chemicals (commodities and high-value products), and materials; and also services (electricity and heat). These plants benefit from the co-production of different kinds of products (low-value high-volume along with high-value low-volume), which enhance the profitability of the plant despite requiring larger and more complex plants. There is potential energy and material integration, because of the combination of routes via a platform chemical: it maximizes the conversion of the syngas and the by-products could be completely converted. The assessment of sustainability means that in the case of the co-production of chemicals, the resulting saving of GHG emissions is the largest, since they are not combusted in their final use. The incorporation of BECCS results in the achievement of negative emissions in the plant. Furthermore, if the biorefinery achieves an extra saving with respect to the regulated emissions for biorefineries, the extra-avoided emissions should also be economically valorized.

Acknowledgements

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Paper 5

Thermochemical biorefinery based on dimethyl ether as intermediate: Technoeconomic assessment

This paper presents the first technoeconomic assessment of a thermochemical biorefinery. It focuses on the conversion of DME via (hydro)carbonylation It has been published as paper in 2013[*]*.*

1. Introduction

The thermochemical conversion of biomass to syngas (gasification) allows catalytic synthesis of chemicals and fuels. A large number of studies have been published on direct synthesis of liquids and gaseous biofuels such as ethanol, Fisher-Tropsch diesel, gasoline and SNG (substitute natural gas). However, studies on the co-production of biochemicals and biofuels via indirect synthesis routes are scarce. Ethanol production from lignocellulosic biomass via dimethyl ether (DME) hydrocarbonylation was assessed by the authors [1], revealing that this indirect route is more cost-competitive than state of the art routes of bioethanol production [1]. This paper explores the potential of such a biorefinery by polygenerating high-value chemical products (methyl acetate and H_2), liquid transportation fuels (ethanol and DME) and electricity. The high-value products enhance profitability, the fuel is helpful to meet national energy needs and the power production reduces costs and avoids greenhouse-gas emissions.

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[*] Haro P, Ollero P, Villanueva Perales AL, Gómez-Barea A. Thermochemical biorefinery based on dimethyl ether as intermediate: Technoeconomic assessment. *Appl Energy*. 2013;102:950-61. DOI: 10.1016/j.apenergy.2012.09.051

Nomenclature

ASU: Air Separation Unit

ATR: Autothermal Reformer

BTL/G: Biomass To Liquids/Gases

CR: Cryogenic Cooling

CW: Cooling water

DCFA: Discounted Cash Flow Analysis

DME: Dimethyl ether

EFG: Entrained Flow Gasifier

HHV: High Heating Value

HP: High Pressure

HRSG: Heat Recovery Steam Generation

iCFBG: Indirectly-heated atmospheric Circulating Fluidized Bed Gasifier

IRR: Internal rate of return

LP: Low Pressure

MA: Methyl acetate

MP: Medium Pressure

NRTL: Non-Random Two Liquid

PSA: Pressure Swing Adsorption

RKS—BM: Redlich—Kwong—Soave with Boston—Mathias alpha function

SNG: Substitute Natural Gas

SR: Steam Reformer

TOC: Total Operation Costs

TPI: Total Plant Investment

TR: Tar cracker/Methane Reformer

Twelve process concepts of the thermochemical biorefinery are assessed and compared. All alternatives use DME as an intermediate. In the first stage, DME is converted into methyl acetate by heterogeneous catalytic carbonylation. The catalyst for this reaction has been recently developed at laboratory scale [2-4]. In the second stage, the methyl acetate is either converted into ethanol and methanol or directly sold as a high-value product[†]. The methanol is converted into DME, increasing the overall ethanol yield. In addition to ethanol and methyl acetate production, the biorefinery concepts considered here include the production of H_2, DME and electricity. The DME can be converted in the plant or sold as a product, the relative proportion of each fraction being determined by the design of the DME conversion section. The production of the other two products, i.e. H_2 and electricity, is selected on the basis of the technology chosen for syngas clean-up and conditioning.

All process concepts have been technically assessed using data both from research literature and technology owners. Economic evaluation is based on data taken from vendors,

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[†] Methyl acetate is currently available as a byproduct of acetic acid production or it can be produced by the esterification of methanol and acetic acid (reactive distillation) [5]. The main uses of methyl acetate are as a solvent (substitute for acetone) [6] and the production of acetic anhydride [7], one of the most important organic intermediates [8].

manufacturers and published BTL/G (biomass to liquids/gases) studies. A sensitivity analysis based on total plant investment (TPI), total operating costs (TOC) and market price of products is also made.

2. Conceptual design of alternatives

Figure 1 shows the scheme of reaction of the species involved in the process (syngas generation excluded). Two main alternatives are shown, according to the DME conversion path: DME carbonylation and DME hydrocarbonylation. The reaction steps involved in Figure 1 are: syngas (CO, H_2) to methanol, dehydration of methanol to DME, carbonylation of DME to methyl acetate, and hydrogenation of methyl acetate to methanol and ethanol.

Production of DME from syngas can be carried out either by direct conversion of syngas (one step) or by methanol synthesis and subsequent dehydration to DME. In this work, the one step process has been selected due to its higher CO per-pass conversion and the availability of technical data.

The catalytic carbonylation of DME over zeolites, e.g. H-Mordenite, has been recently demonstrated at lab scale [9-11]. Methanol can also be carbonylated to methyl acetate, but deactivation of the catalyst by the generated water occurs. The hydrogenation of acetates is a well-known process for which different catalysts have been developed [2-4, 12-14]. In this work, data from various recent developments have been considered: (i) for the hydrocarbonylation cases a combination of a carbonylation (H-Mordenite) and a hydrogenation (Cu-ZnO) catalyst is used. The performance of these catalysts has been successfully tested in a dual fixed bed reactor fed with syngas and DME [2-4], whereas the technical considerations are taken from [1]; (ii) experimental data and reactor conditions for DME carbonylation, are taken from [4]. These studies have shown that a large excess of CO in the reactor is necessary for both hydrocarbonylation and carbonylation of DME. Therefore, in the present work, these ratios are used: CO/DME molar ratio of 10 for hydrocarbonylation [3] and of 47.1 for carbonylation [4].

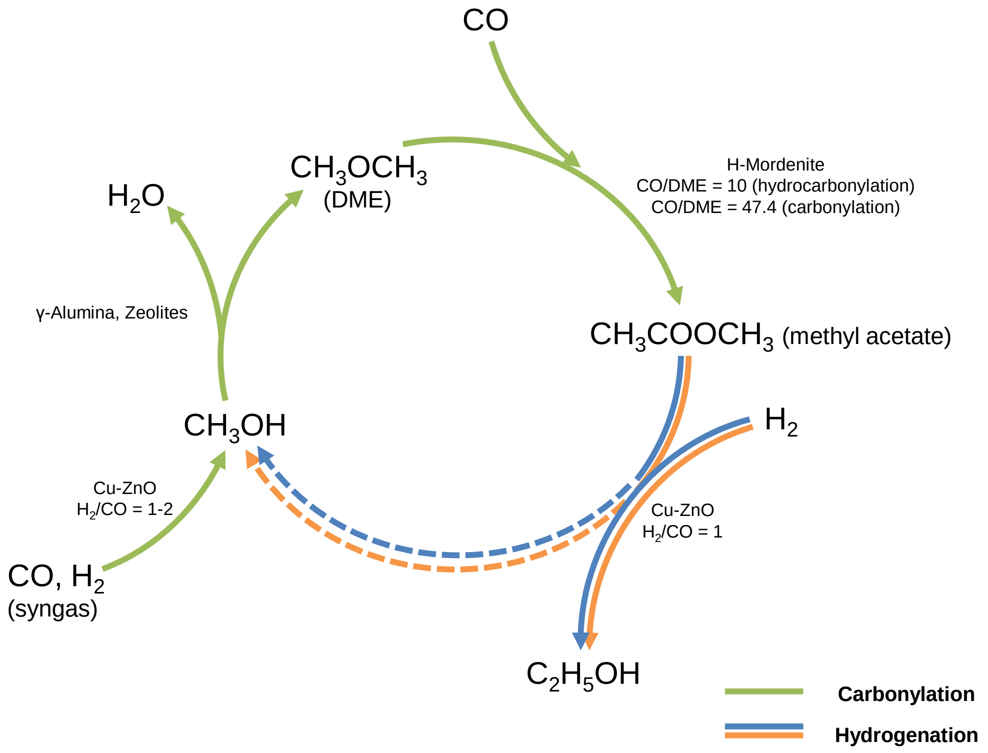

Figure 1. Chemical scheme illustrating the routes from syngas to different products through DME. The two main DME conversion routes are shown: carbonylation and hydrocarbonylation (carbonylation followed by hydrogenation). Dashed lines refer to the possibility of “extra” methanol dehydration to DME through methanol synthesis.

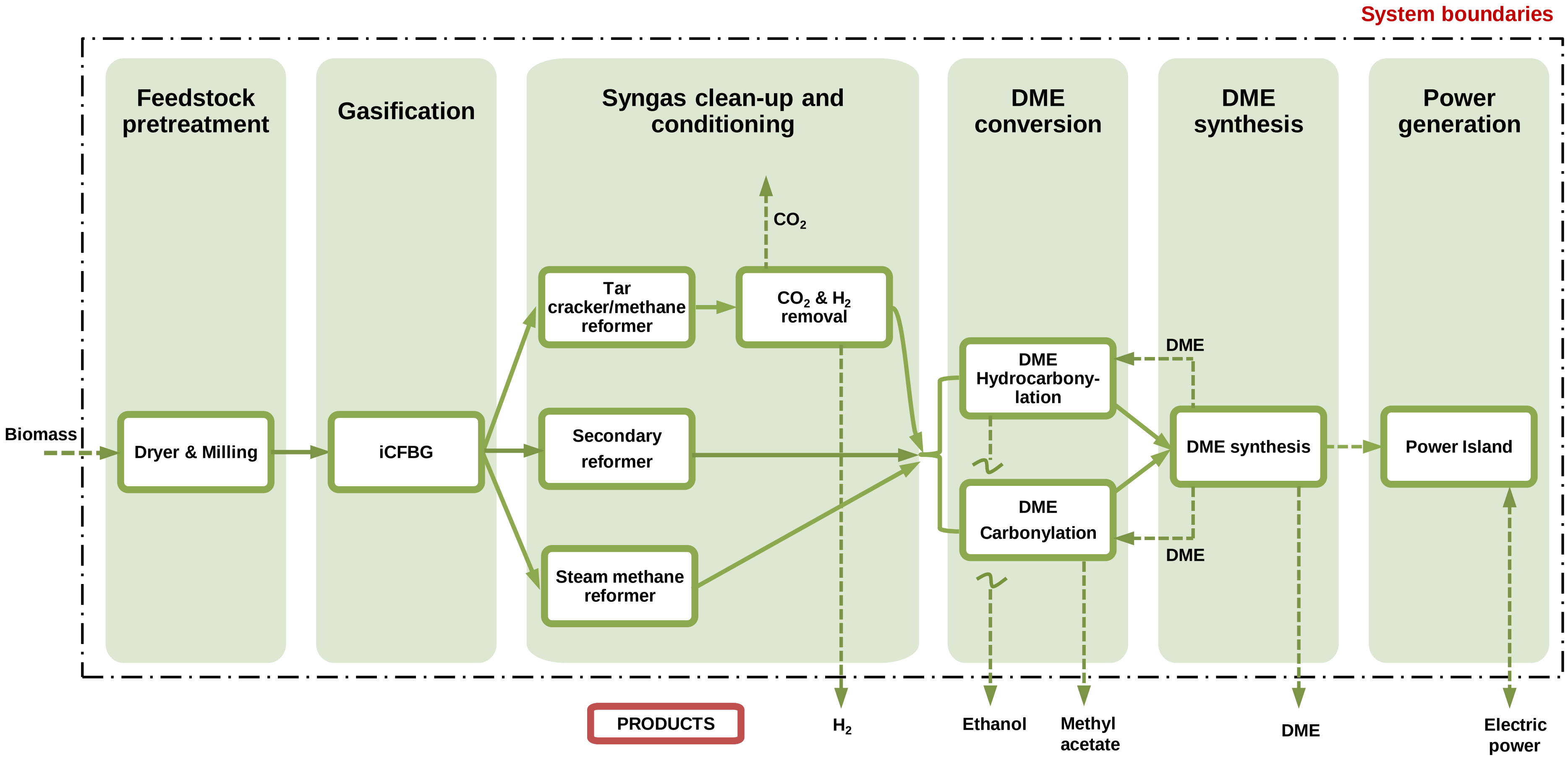

Figure 2. Layout of the process concept alternatives analyzed in the present work.

Figure 2 shows the layout for considered process concepts. Pretreated biomass is converted into syngas in an indirectly-heated circulating fluidized bed gasifier (iCFBG) operated at atmospheric pressure. The raw syngas is cleaned-up and conditioned. Three alternatives have been considered for these processes: a steam reformer (SR), a secondary autothermal reformer (*secondary*-ATR) and a tar cracker/methane reformer (TR). In the case of TR, the syngas has to be conditioned by CO_2 and H_2 removal (recovery) systems in order to meet the requirements of the synthesis catalytic reactor. The recovered H_2 can be sold or sent to a gas turbine for power generation, leading to two different alternatives.

After the upgrading stage, the syngas is sent to the DME conversion section. This is the main difference of the present approach compared to conventional processes, where syngas would be sent to a DME synthesis section. The ground relies on the large excess of CO required in the DME conversion reactor. In the case of the DME synthesis section prior to the conversion section, the total amount of CO would not be enough to achieve the required CO/DME ratio without recirculation of the unconverted syngas in the conversion loop. Hence, if the fresh syngas is used in the DME conversion section, it is found that there is still enough for DME synthesis, it avoids syngas recirculation to produce methyl acetate/ethanol (no recycle-compressor is necessary) and reduces some operating costs, e.g. the syngas should not be compressed to the DME synthesis pressure (50 bar), but only to the DME conversion pressure (10-30 bar).

For the DME conversion section, two alternatives are considered, i.e. DME carbonylation and hydrocarbonylation leading to the 6 different process alternatives up to this point (by considering the upstream options for the syngas upgrading). For the DME hydrocarbonylation concepts, we have considered two additional alternatives: extra production of DME or higher power generation, leading to a total of 12 process concepts. In the case of the DME hydrocarbonylation concepts, the produced methanol is always removed by condensation and sent for dehydration in the DME synthesis reactor.

For all process concepts, the gas from the DME synthesis reactor and other gas streams produced in the process are used to produce power and to satisfy the heat demand. Some alternatives produce an excess of electricity, i.e. more than that required for self-consumption, so there is a net power production, whereas other concepts need to import power.

To sum up, the products considered in the present work are:

- **Methyl acetate**. Produced within DME carbonylation concepts. The production is determined by the design of DME conversion section.
- **Ethanol**. Produced within DME hydrocarbonylation concepts. The production is determined by the design of DME conversion section.
- **H_2**. Produced only in TR concepts, where the H_2 in the syngas is in excess with respect to that required for DME hydrocarbonylation and DME synthesis.
- **DME**. It is considered as an alternative for DME hydrocarbonylation concepts and it is always produced in DME carbonylation concepts. The DME product achieves commercial grade and can be directly sold in the market.
- **Electric power**. Produced in some process concepts as a result of process configuration selected for some alternatives.

3. Detailed design and description of alternatives

3.1. Basis for design

The system boundaries for the process concepts considered are shown in Figure 2. The design basis and inputs are shown in Tables 1 and 2. For all alternatives the biomass feedstock is poplar chips. Table 1 also includes the design basis used in literature studies for comparison. Detailed data is presented in the Supplementary Information.

Table 1. Design basis for the alternatives of this work together with others taken from the literature.

	This study	**[1]**	**[15]**	**[16]**
Feedstock	Poplar chips	Poplar chips	Poplar chips	Hybrid poplar
Plant size (dry tonnes/day)	2140	2140	2140	2000
Plant size (MW_{th} on HHV basis)	500	500	500	466
Gasifier	iCFBG	iCFBG	EFG	iCFBG
Energy self-sufficient criterion [a]	No	Yes	Yes	Yes
Electrical energy neutral criterion [b]	No	Yes	Yes	Yes
Feedstock price (USD_{2010}/dry tonne)	66	66	66	51
Target	Polygeneration	Ethanol	Ethanol	Ethanol

HHV: high heating value; EFG: entrained flow gasifier.

[a] The energy self-sufficient criterion means that the only energy input is biomass.

[b] The electrical energy neutral criterion means that the required power is produced within the plant.

Table 2. Properties of biomass feedstock (poplar chips).

Component	% wt, dry basis
Carbon	50.90
Hydrogen	6.05
Oxygen	41.92
Nitrogen	0.17
Sulphur	0.04
Ash	0.92
Moisture	30% wt
HHV	20.18 MJ/kg

3.2. Process description

The thermochemical biorefinery concepts are compiled in Table 3, along with their assigned codes. Process alternatives for each one are also identified.

Table 3. Definition of the biorefinery process concepts.

	SR-01	**SR-02**	**SR-03**	**ATR-01**	**ATR-02**	**ATR-03**	**TR-01**	**TR-02**	**TR-03**	**TR-04**	**TR-05**	**TR-06**
Product												
Methyl acetate			✓			✓					✓	✓
Ethanol	✓	✓		✓	✓		✓	✓	✓	✓		
H_2								✓		✓	✓	
DME		✓	✓		✓	✓			✓	✓	✓	✓
Electric power	✓	✓	✓	✓	✓	✓	✓	✓	✓	*	*	✓
Process alternatives												
Steam reformer (SR)	✓	✓	✓									
Secondary reformer (*secondary*-ATR)				✓	✓	✓						
Tar cracker/methane reformer (TR)							✓	✓	✓	✓	✓	✓
CO_2 removal system							✓	✓	✓	✓	✓	✓
H_2 separation unit							✓	✓	✓	✓	✓	✓
DME Carbonylation			✓			✓					✓	✓
DME Hydrocarbonylation	✓	✓		✓	✓		✓	✓	✓	✓		

The concepts marked with * require an external supply of electric power.

3.2.1. Feedstock pretreatment

Biomass feedstock with 30 wt% moisture is dried in a rotary dryer, where moisture is reduced to 12 wt% with combustion gases from the gasifier (iCFBG). The gas has been previously cooled from 800°C down to 450ºC to produce high pressure (HP) steam in a heat recovery steam generator (HRSG). Dried poplar chips are sent to a hammer mill for particle reduction below 4 cm.

3.2.2. Gasification

For the synthesis of liquid fuels and other chemicals only a nitrogen-free syngas is suitable. Three gasification technologies can be considered: (a) EFG, (b) CFBG with O_2 and steam and (c) iCFBG using air and steam. The first two technologies are directly-heated oxygen-blown gasifiers, whereas the third operates with air and does not need an ASU (air separation unit) plant. EFG and iCFBG have been previously considered in prior studies aimed at ethanol production [15, 17]. An EFG was disregarded because processes based on this gasifier were found to be more expensive than those based on iCFBG for all alternatives analyzed [17]. The selected atmospheric iCFBG was modeled considering experimental data [18]. The performance data of the iCFBG is shown in Table 4.

Table 4. iCFBG operating parameters, exit gas composition and efficiency.

Gasifier Performance[a, b]	
Pressure	1.5 bar
Temperature	900 ºC
Steam (2 bar, 140ºC)/dry Biomass	0.4 kg/kg
Heat loss in gasifier	1.53% HHV
Cold gas efficiency (%HHV)	77.07
Component	mole (%)
H_2	14.55
CO	23.64
CO_2	6.92
H_2O	43.43
CH_4	8.43
NH_3	0.18
Tars	0.15
C2+	2.70
H_2S	184 ppm

[a] Dust, nitrogen and alkali compounds, and halogens are not included.

[b] Case of tar recirculation to the combustor of the gasifier; when there is no tar recirculation to combustor, raw syngas flow and composition change according to iCFBG model.

3.2.3. Gas clean-up and conditioning

The raw syngas from the gasifier contains dust, tars, nitrogen and alkali compounds, and halogens which must be removed in order to prevent damage to equipment and the poisoning of catalysts. Two possibilities to remove the tars from the raw syngas are considered: (1) oil and water scrubbing (for SR and ATR concepts), and (2) TR along with water scrubbing. Removal of particles is carried out in both cases by high-temperature cyclones. Sulphur compounds (H_2S and COS) are removed by a liquid phase oxidation process (LO-CAT®) and bed filtration (ZnO). The syngas is then conditioned to meet the requirements of the downstream catalysts in the reaction loop: a H_2/CO ratio of 1, a low content of CO_2 (<10%v/v) and hydrocarbons (mainly methane) in the DME conversion section, and syngas dewatering. For tar and light hydrocarbon reforming some alternatives have been studied in previous BTL/G publications (SR, ATR and TR, used alone or in combination with removal systems for H_2 and CO_2) [15, 16, 19-28]. In this work, three alternatives for syngas reforming are considered: SR, secondary reformer (*secondary*-ATR) and TR. These processes have been modeled using technical data of natural gas reforming (for SR and *secondary*-ATR) and experimental data (for the TR) [29].

3.2.3.1. Steam Reforming (SR)

In these concepts the gas from the gasifier is de-dusted in a high efficiency cyclone and cooled down to 400ºC in a HRSG. Then it is sent to an OLGA™ system where tars are removed by oil-scrubbing [30]. Collected tars and waste solvent are recycled and burned in the riser (combustor) of the gasifier. Nitrogen compounds, alkalis and HCl are removed by water scrubbing. The cleaned syngas is compressed up to 17 bar and desulphurized in the LO-CAT® system where H_2S is oxidized to elemental sulphur [31, 32]. The concentration of H_2S is further reduced in a Co-Mo/ZnO dual bed, where hydrogenation of olefins into paraffins also takes place. The desulphurized syngas enters the SR where methane and light paraffins are converted into syngas. The H_2/CO ratio is adjusted by setting the steam to hydrocarbon ratio, ensuring no carbon deposition over the catalyst. The reformed syngas is cooled, compressed and dehydrated in a molecular sieve, preventing the presence of water in either the DME hydrocarbonylation or in the DME carbonylation reaction section [1].

3.2.3.2. Autothermal Reforming (ATR)

The alternatives using ATR have the same cleaning system as those for SR. The *secondary*-ATR reformer is a mature technology for gas streams with a low hydrocarbon content [25]. Both steam and oxygen are fed to the secondary reformer, which operates at 32 bar. Due to the low consumption of oxygen in the secondary reformer, oxygen production in an ASU plant is not considered, but the oxygen is imported.

3.2.3.3. Tar Reforming (TR)

The raw syngas enters the TR free of particles. Design of this system is made on the basis of recent experimental data [29] obtained for a given catalyst and operating temperature (see Supplementary Information for more details). The outlet stream is cooled and the remaining impurities (dust, alkalis, residual ammonia, etc.) are removed by water scrubbing. Then, the cleaned syngas is compressed and desulphurized as in SR-concepts.

3.2.3.4. Removal of CO_2 and H_2

The CO_2 and H_2 removal (recovery) is not carried out in process alternatives with SR or secondary reformer, since both reforming technologies allow adjustment of the steam to hydrocarbon ratio. In TR cases, the steam to hydrocarbon ratio is determined by the gasifier; the CO_2 concentration in the syngas is high and the H_2/CO ratio is about 1, close to that required in the process. For example, in the TR-03 concept (production of ethanol, DME and electric power), the CO_2 concentration in the DME synthesis loop accumulates up to 52%v/v if CO_2 is not removed, resulting in the necessity of large equipment. The selected technology for CO_2 removing is an amine system, due to the low partial pressure of CO_2 in the gas. A PSA (pressure swing adsorption) system is selected for recovering the excess of H_2. This H_2 may be sold as a product or burned in gas turbine for power generation.

3.2.4. DME conversion section

As described above, there are two alternatives depending on whether DME hydrocarbonylation or DME carbonylation is applied. In all cases, the DME conversion section is designed as multi-stage reactors with DME shots. In the cases based on DME hydrocarbonylation, there are also inter coolers and gas-liquid separators, as shown in Figure 3. This configuration fits process requirements best because it enables high DME conversion in the reactor and does not require syngas recirculation to fulfill the high CO/DME ratio required, like in the case of using a single reactor. For the DME hydrocarbonylation concepts, the recovery of liquid products (ethanol and methanol) is necessary in order to avoid degradation of products in the next reactor stage. As shown in Figure 3, conditioned and dewatered syngas is fed to the first stage together with the corresponding amount of DME. In this work, a reactor with 5 stages has been selected for both DME carbonylation and hydrocarbonylation.

3.2.4.1. DME hydrocarbonylation

For the design of the DME hydrocarbonylation section, a CO/DME ratio of 10 was used on the basis of recent results [1]. Collected liquid products from the reactors (methanol, ethanol and small amounts of methyl acetate) are mixed and sent to the product separation section.

3.2.4.2. DME carbonylation

For the design of the DME carbonylation section, all concepts are designed and modeled using a CO/DME ratio of 47.1 in the presence of H_2. Methyl acetate and some ethyl acetate are recovered by cryogenic cooling and sent to the product separation section.

3.2.5. DME synthesis

The DME synthesis section is modeled using information of the JFE's process [33], in which syngas with a high CO_2 content is processed, like in the present work. In the one step DME reactor, CO, H_2 and some CO_2 are converted into DME, and methanol and water to a lesser extent. The catalyst used in the JFE process is a dual catalyst, i.e. Cu-ZnO and a kind of zeolite or alumina, suspended in a solvent (slurry reactor); one catalyst synthetizes methanol from syngas and the other dehydrates the methanol to DME. A variable amount of methanol can be fed to the reactor and converted into DME by adjusting the dual catalyst proportion [33]. Therefore, extra methanol can be converted to DME in the reactor [33]. Moreover, the Cu-ZnO catalyst is the same as (or close to) that used in the hydrocarbonylation reactor, so methyl acetate is assumed to be completely hydrogenated into methanol and ethanol in the DME synthesis reactor.

In the DME synthesis section, there are two alternatives for the processes based on DME hydrocarbonylation. The unconverted syngas from the DME conversion section can be used to produce either the amount of DME necessary for ethanol production or further DME. The latter is carried out by syngas recirculation in the DME synthesis section, or removing purge after the DME conversion section. In the DME carbonylation-based concepts, there is always a net production of DME due to the larger CO/DME ratio required. A larger CO/DME ratio causes lower methyl acetate generation compared to the case of DME hydrocarbonylation, leading to larger amounts of unconverted syngas in the DME synthesis section. In this case, the maximization of DME production results in high production of DME (the main product in terms of mass production).

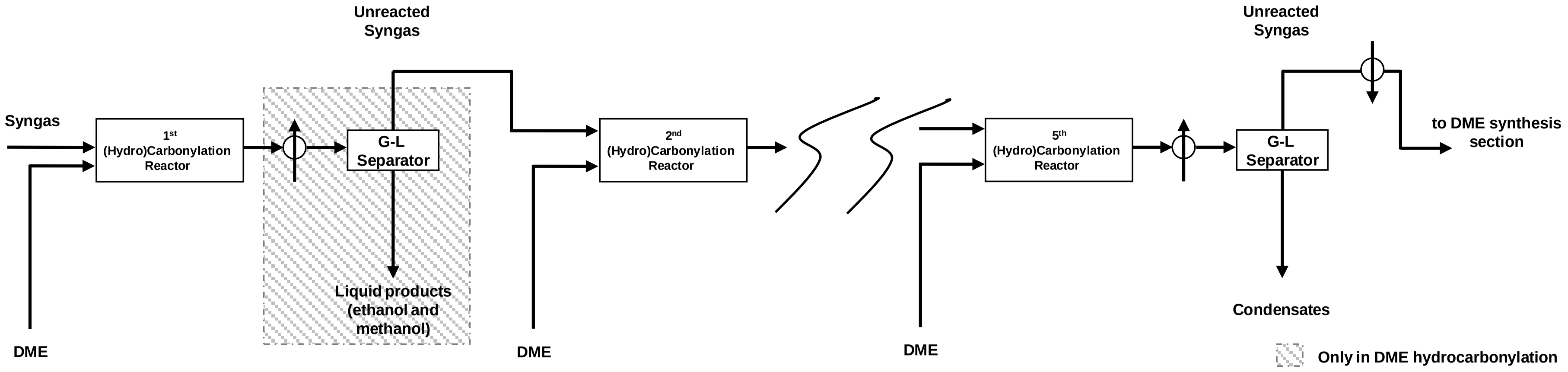

Figure 3. Configuration for the DME conversion section.

3.2.6. Product separation

The design of the product separation section depends on whether there is a DME hydrocarbonylation or a carbonylation process concept. In the first case, the liquid products are ethanol, methanol and, to a lesser extent, methyl acetate. Methyl acetate is first removed along with dissolved gases by means of a stabilizer column and recycled to the hydrocarbonylation reaction section for complete conversion to alcohols. Then, ethanol is distillated to meet fuel-grade specifications and the methanol recycled to the DME synthesis section, where it is dehydrated in the reactor by adjusting the proportion of dehydration catalyst.

In the case of alternatives using DME carbonylation, the produced methyl acetate is recovered in a stabilizer column as liquid distillate. The outlet stream from the DME synthesis reactor is condensed and CO_2 is recovered by distillation in a stabilizer column. Methanol is separated from water by distillation and recycled to the DME synthesis reactor. In concepts where DME is produced, the product stream contains around 99.0-99.5%v/v of DME, with CO_2 and methanol as the main impurities. The effluent from the DME carbonylation and the effluent from the DME synthesis reactor are cooled using the cryogenic refrigeration (CR) system.

3.3. Energy balance and integration

In most cases, the off-gas streams, mainly those coming from the DME synthesis loop purge and the vapor distillate from the DME conversion section, are enough to make the process energy self-sufficient with some power production. Only in two of the twelve cases is the power balance of the plant negative (TR-04 and TR-05 concepts) and does electricity have to be imported. For all cases, except SR-02, a combined cycle is considered for power production (see Table 3).

3.4. Process flow diagram of the cases analyzed

As examples, the process flow diagram for cases SR-01 and TR-06 are shown in Figures 4 and 5. The process flow diagrams of all process cases analyzed along with modeling details of the main equipment are presented in the Supplementary Information.

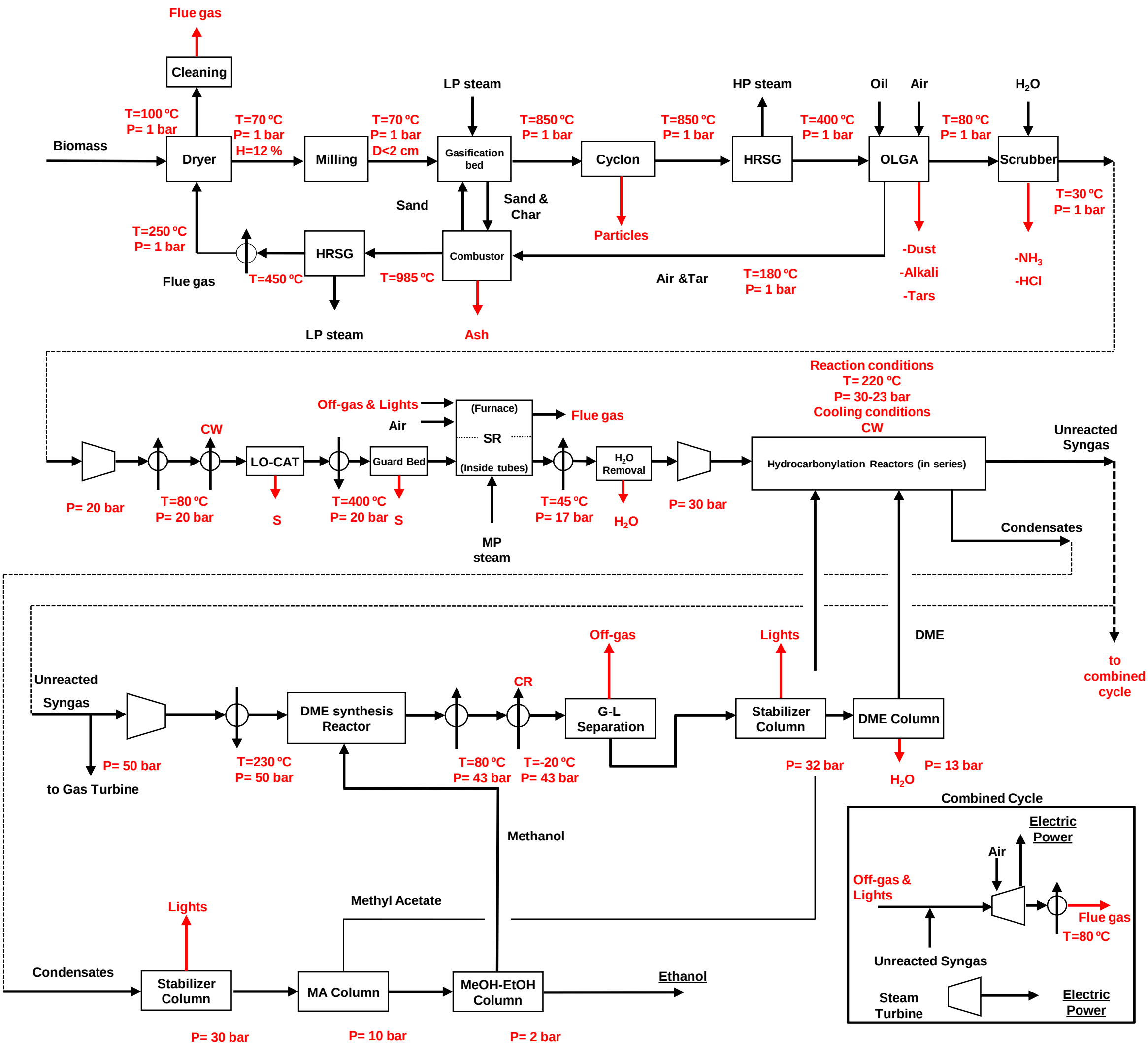

Figure 4. Process flow diagram for SR-01.

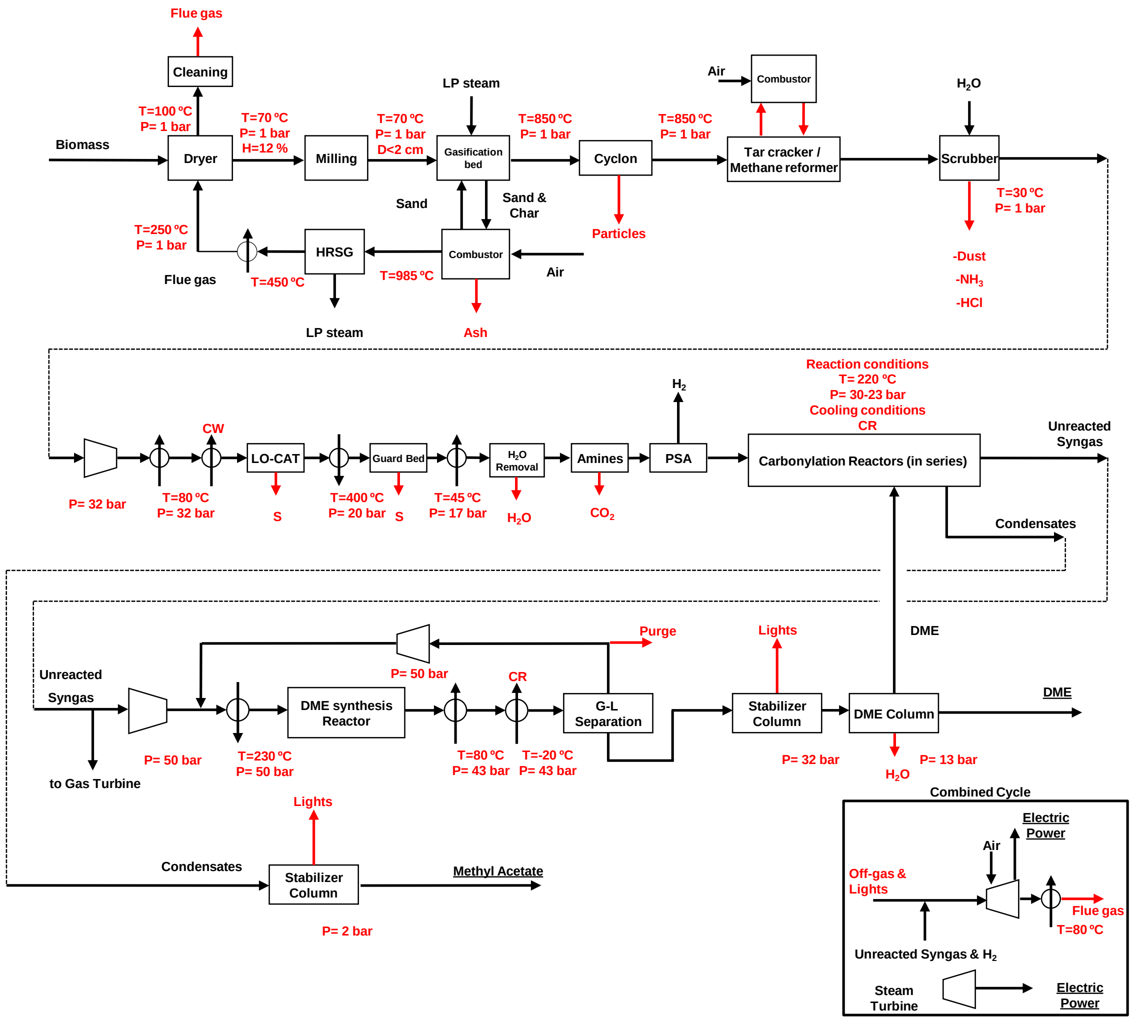

Figure 5. Process flow diagram for TR-06.

4. Further aspects on process modeling

Process concepts are modeled in Aspen Plus process simulator. The modeling parameters and assumptions of process units are presented in detailed in the Supplementary Information. Only the most important considerations are included in the following.

4.1. Thermodynamic modeling

Two thermodynamic models have been used to model the process concepts. For gasification, gas clean-up and conditioning, the DME conversion and DME synthesis reaction sections, the equation of state of Redlich—Kwong—Soave with Boston—Mathias alpha function (RKS—BM) was used. The Non-Random Two Liquids (NRTL) method with the Redlich-Kwong equation of state was used to simulate the product separation section.

4.2. Modeling and estimations of the economics of the process

The assumptions for the discounted cash flow analysis (DCFA) are shown in Table 5. The internal rate of return (IRR) of each process concept is calculated by setting the market price of products in the DCFA. Table 6 shows the market prices in the economic scenario assumed. Further information of the economic methodology is included in Supplementary Information.

Table 5. Economic assumptions for discounted cash flow analysis.

Parameter	Value
Debt/Equity	0/100%
Plant life	20 years
Depreciation (linear)	10 years
Salvage value	0 M USD
Construction period	1 year
Income tax	30%
Working capital	1-month operating costs
Land	6% TIC

Working capital and cost of land are recovered at the end of plant life.

Table 6. Commercial prices of products for the economic assessment.

Product		References
Ethanol (USD_{2010}/L)	0.61	[34]
Methyl acetate (USD_{2010}/L)	1.71	[35]
H_2 (USD_{2010}/kg)	1	[36]
DME (USD_{2010}/m^3)	692	internal communication
Electric power	5 $cUSD_{2010}$/kWh	assumed

5. Results and discussion

5.1. Energetic efficiency

Figure 6 shows the energy efficiency calculated for the 12 cases. The efficiency is defined in Eq. (1), where a transformation factor of 0.39 was assumed to translate MW_{th} to MW_e. The energy content in the various energetic vectors (products), i.e. ethanol, MA, DME, H_2 and electricity is indicated. As can be seen, electric power is a product in 10 cases, whereas there are two cases (TR-04 and TR-05) where it is imported. When extra power is required, the extra energy input is added to that of the biomass.

$$Energy\ efficiency = \frac{HHV\ of\ products\ (MW) + electricity\ generated\ (MW)}{HHV\ of\ biomass\ (MW) + \frac{electricity\ consumed\ (MW)}{0.39}} \qquad (1)$$

Greatest energy efficiency is achieved by TR-02 (50.24%), where ethanol, H_2 and electric power are produced, whereas lowest energy efficiency (34.89%) corresponds to TR-03, where ethanol, DME and electric power are produced. There is no correlation between process alternatives (syngas upgrading technology, DME conversion route) and the resulting energy efficiency of process concepts.

Figure 7 shows the power sinks and sources in the alternatives analyzed. The power sinks are grouped in their corresponding process section while the power sources are directly identified. Most of the power is demanded by the clean-up and conditioning section. *Other consumptions* in the figure refers to the power demand in cryogenic refrigeration, which is the largest consumption in this group. In the power generation section a gas turbine is presented in all concepts. Thermal integration is satisfied by the steam generated within the system boundaries, including that generated in the HRSG after the gas turbine. Such a constraint makes production of extra steam impossible for power generation in SR-02 case.

Both the TR-01 and TR-06 concepts generate the highest amount of power and are also the process alternatives with the highest net electricity production. The SR-02 and TR-04 cases produce the lowest amount of power.

5.2. Economics

The economic results for all process concepts are presented below. Sensitivity analysis for some concepts, in terms of TPI and TOC, is also provided.

5.2.1. Analysis of the base case

Figure 8 shows the total operating costs (TOC) calculated for cases SR-01, ATR-03, TR-01 and TR-06, which are a representative sample of the 12 process concepts considered in this assessment. The TOC is similar for all cases, ranging from 78 (SR-01) to 90 (ATR-03)

$MUSD_{2010}$/year. The cases based on ATR consume oxygen, increasing the TOC compared to other cases. Figure 9 shows the total plant investment (TPI) for each process alternative. The TPI ranges from 355.57 (ATR-02) to 552.74 (TR-06) $MUSD_{2010}$. This variation is mainly due to the size of the DME synthesis and Power Island sections. The cases based on DME carbonylation produce DME, increasing the investment costs in the DME synthesis section. The process alternatives producing high amounts of electricity (TR-01, TR-03 and TR-06) also have higher TPI's due to the larger, i.e. more expensive, Power Island.

The IRR of the alternatives is shown in Figure 10. The maximum IRR corresponds to the ATR-03 (28.74%), being significantly larger than the conventional value usually assigned in similar BTL/G studies (IRR = 10%) [1, 15-18] when computing the minimum selling price of products. The highest IRR was computed for cases based on DME carbonylation. However, the internal rate of return for DME hydrocarbonylation concepts producing ethanol is around 10% for cases with SR, slightly below 10% for cases with ATR and quite low for cases with TR.

5.2.2. Sensitivity analysis

Figure 11 shows the sensitivity of the IRR to a change in the TPI of ±30% expected accuracy of a typical study estimate [37] for SR-01, ATR-03, TR-01 and TR-06 concepts: a representative sample. The same change (±30%) is used for the TOC and market price of products. The main uncertainty in the TPI is the investment cost of the gasifier and reforming technology, whereas in the TOC it is the cost of the biomass. For the market price of products, uncertainty is hard to assess accurately. Hence, it has been assumed to range equal as the TPI and TOC.

The trend is similar for both the TPI and TOC: the impact on the internal rate of return amounts to a maximum variation of +12/-10 points. The impact is similar for the market price of each product. Nevertheless, more volatility might be expected for the commercial price of products, increasing the impact on the internal rate of return.

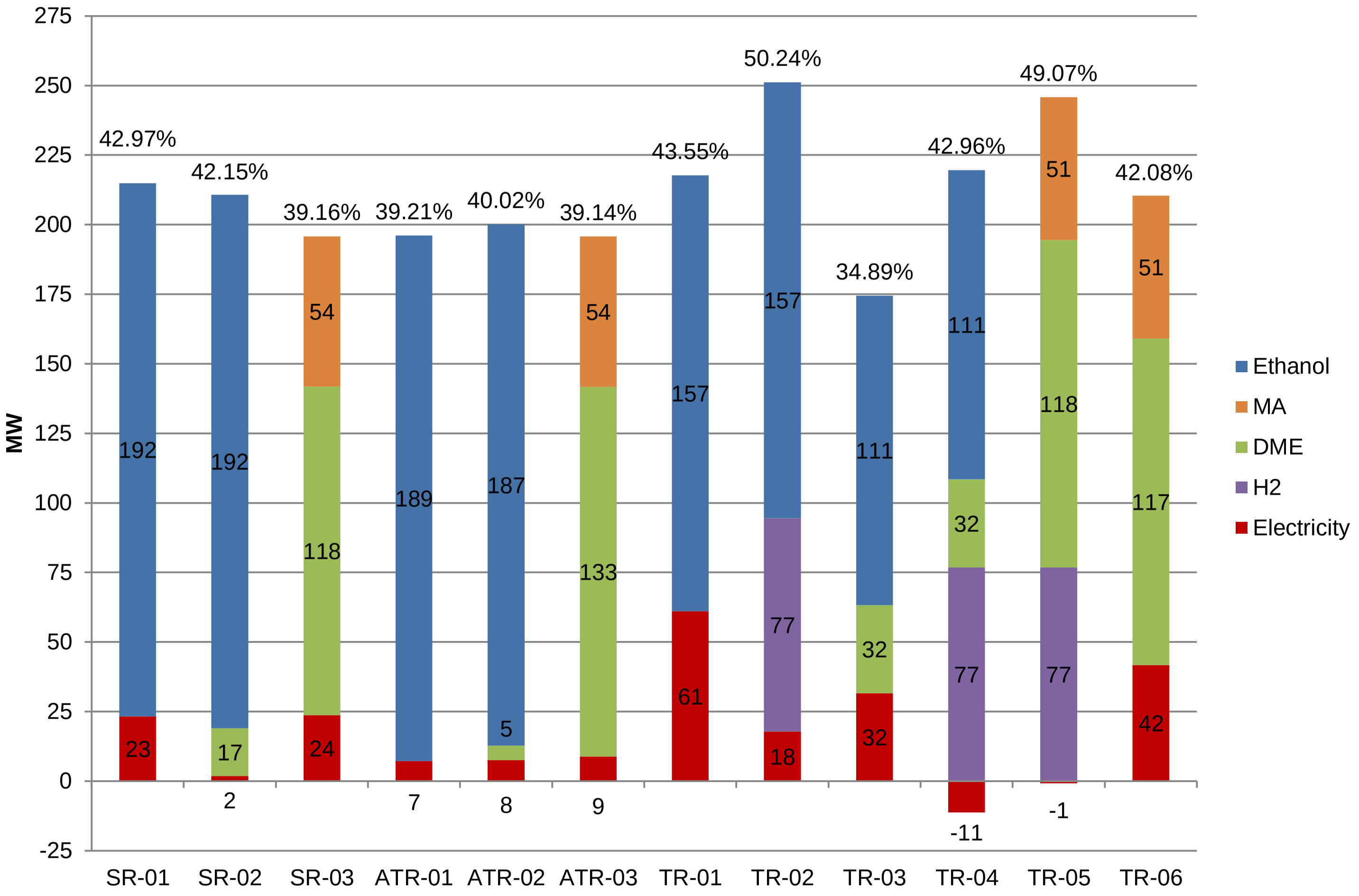

Figure 6. Global energy efficiency (%HHV) and energy content to products (in MW) for each process concept.

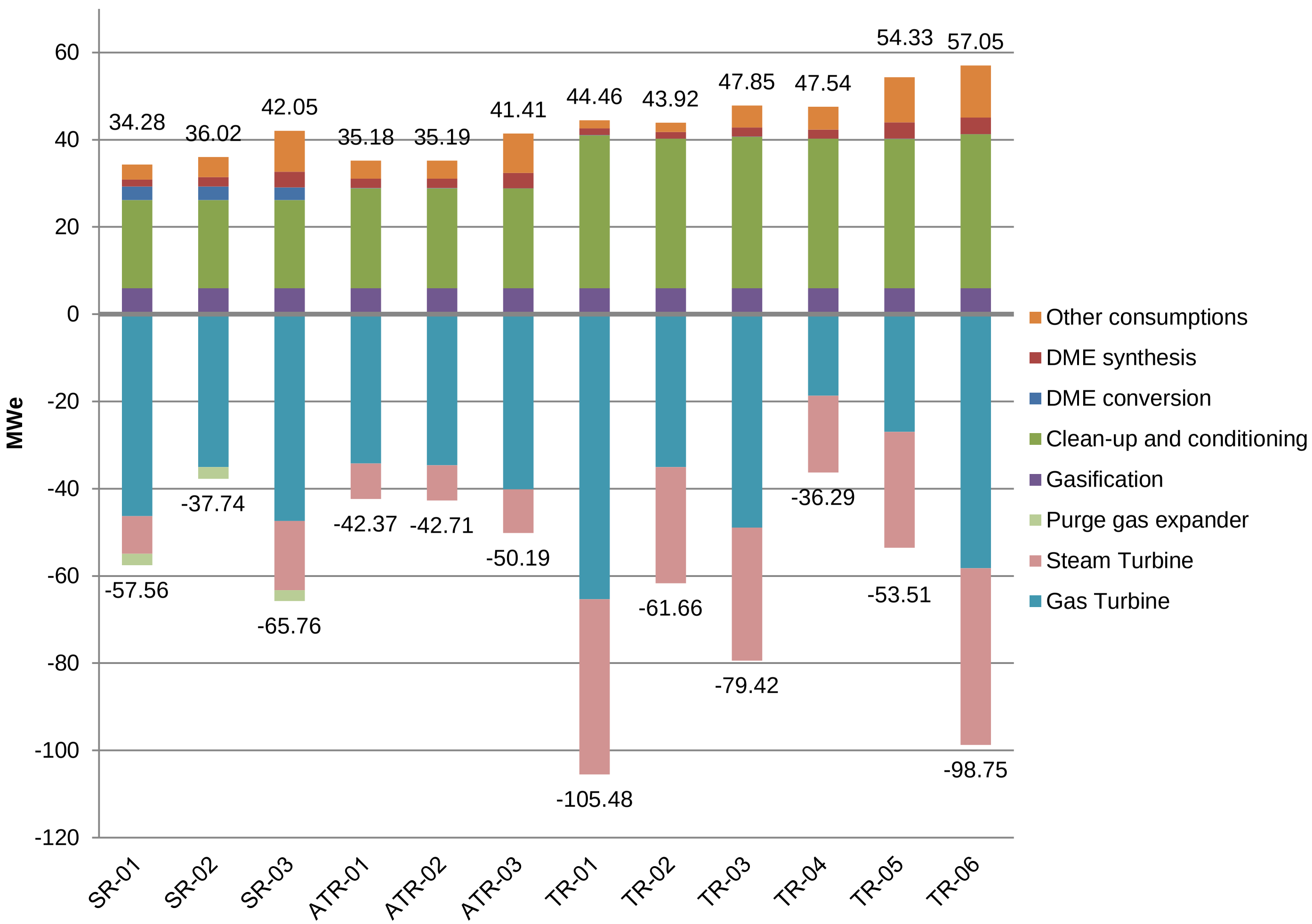

Figure 7. Power consumption and generation for the cases analyzed.

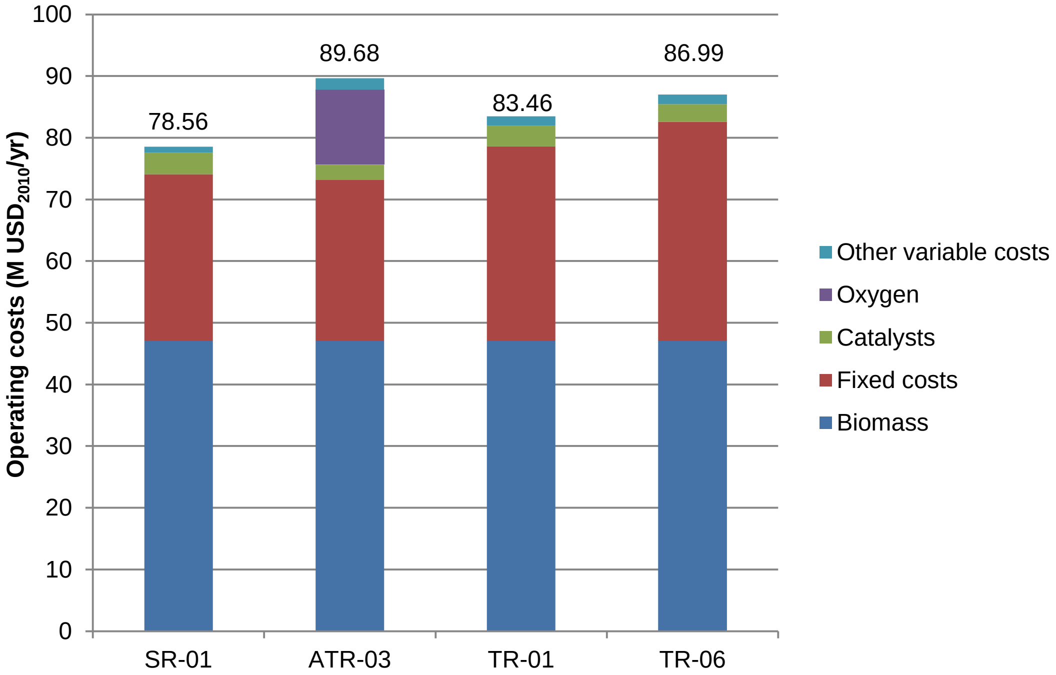

Figure 8. TOC for some assessed process concepts.

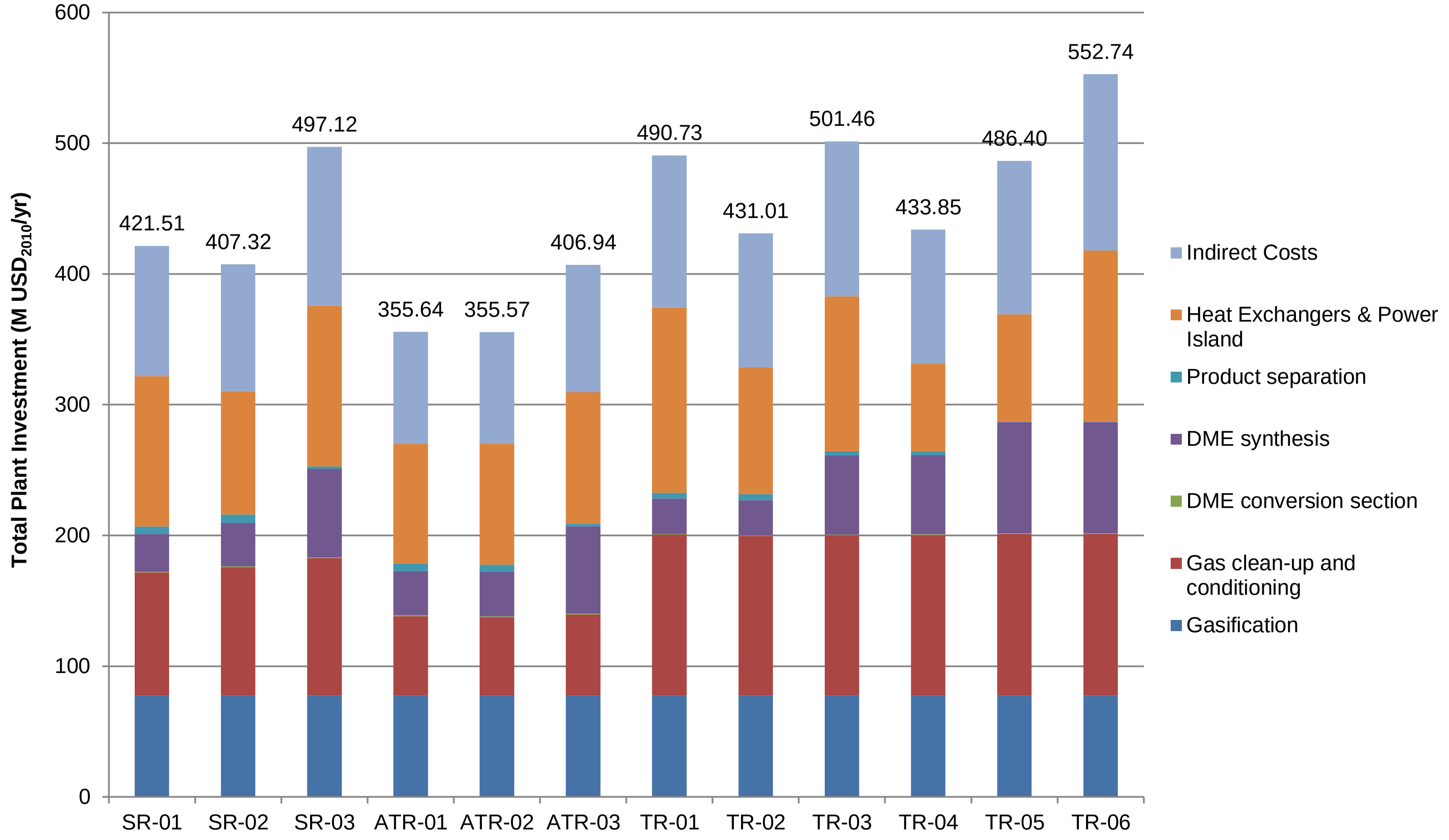

Figure 9. TPI for each assessed process concept.

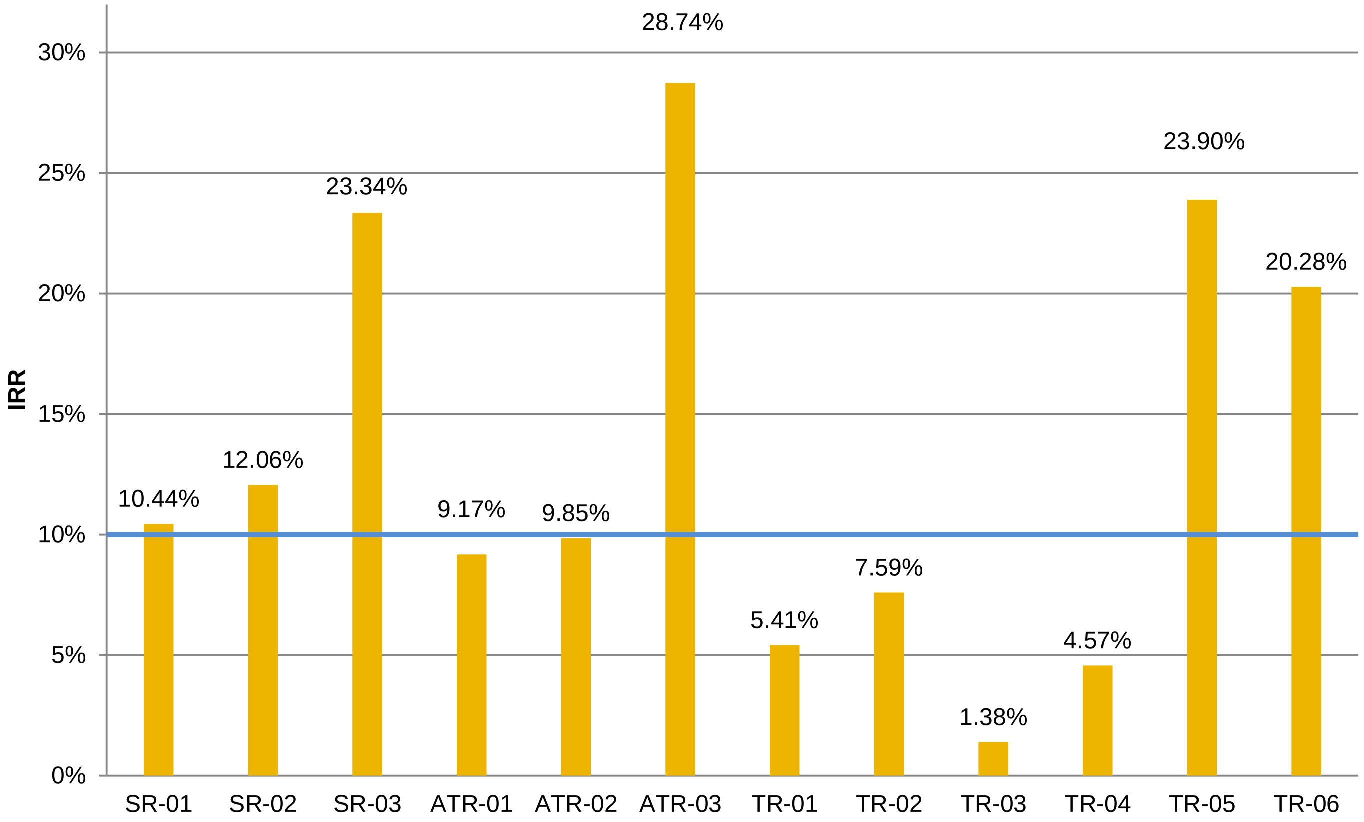

Figure 10. Internal rate of return of each process concept.

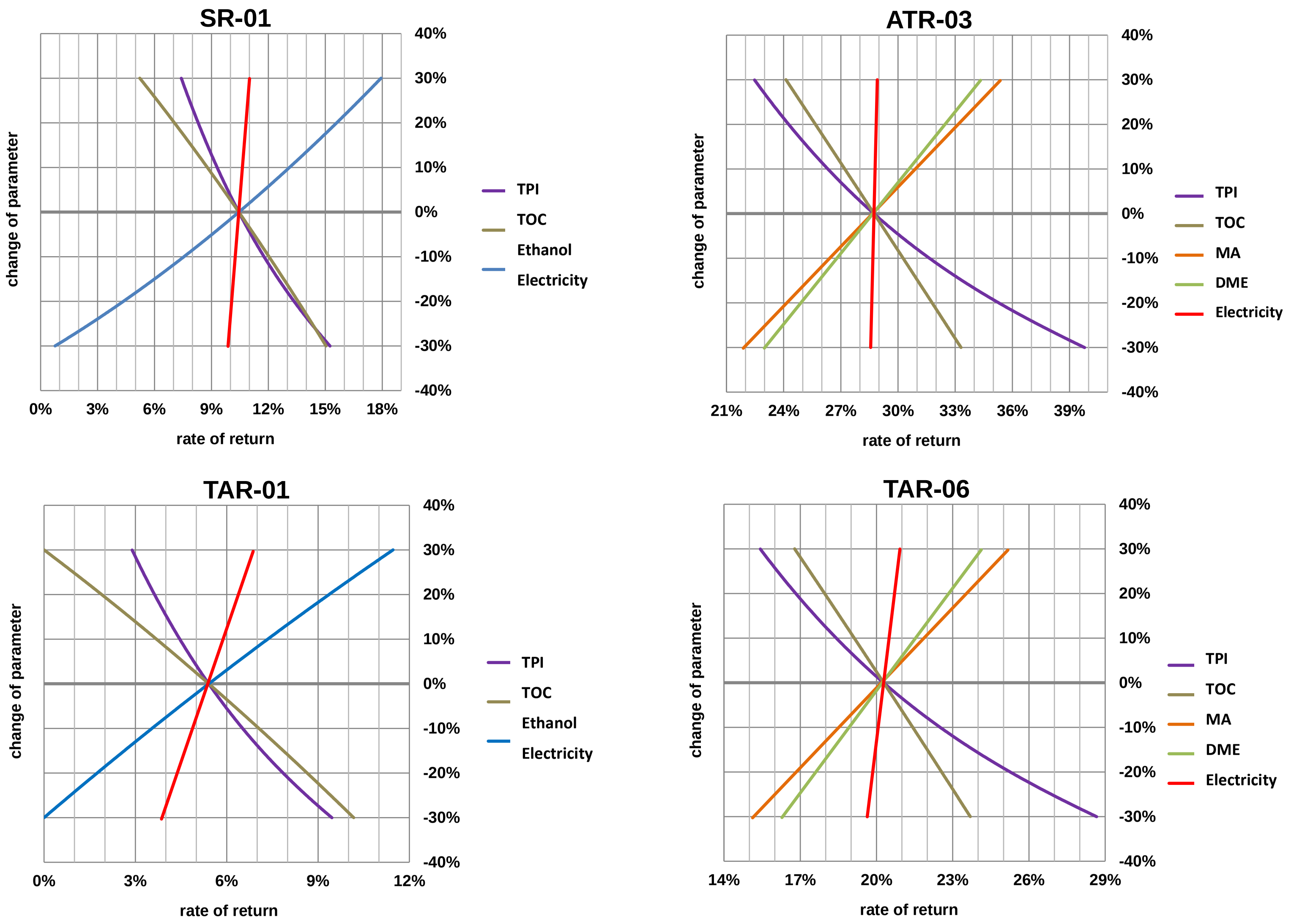

Figure 11. Sensitivity analysis for some assessed concepts.

5.3. Discussion

In this paper, special attention to both energetic efficiency and rate of return is given as they are critical for a comprehensive comparison of BTL/G processes. The feasibility analysis of new production processes requires evaluation of these indicators in order to select the most promising options. The energetic efficiency enables the comparison with competing BTL/G or analogous petrochemical processes. In this work, the resulting energetic efficiencies are close or even greater than those reported in similar BTL/G assessments [1, 15, 16]. However, the energetic efficiencies of dedicated DME [38-40] and methanol [40, 41] production processes are slightly higher than our best biorefinery concept. The lower energetic efficiency obtained in this work is justified by the additional conversion steps necessary to transform DME into derived-products. The rates of return obtained in the cases of DME carbonylation reveal that the combination of high biomass price and methyl acetate selling price does not make critical the TPI of the plant, so economic feasibility of the process can be achieved. These obtained rates of return differ significantly from previous BTL/G studies. In the cases of DME hydrocarbonylation the high biomass price and moderate commercial price of ethanol makes the TPI critical, so the feasibility of the process is questionable. Furthermore, the TPI is very sensitive to variations of the ethanol price.

6. Conclusions

Twelve process concepts based on DME as an intermediate are technoeconomically assessed, considering both the carbonylation and hydrocarbonylation of DME for commercial proposes. The assessment includes biomass pretreatment, gasification, syngas upgrading, DME synthesis and conversion, product separation and heat and power integration. Process alternatives considered in this study (Table 3) are made according to current and future market development for both technical viability and economic feasibility of a thermochemical biorefinery at medium term.

The results of this study establish that a thermochemical biorefinery based on DME as an intermediate achieves similar energy efficiencies to other BTL/G studies [16, 19, 23, 24, 26, 28], i.e. from 35 to 60%. The calculated TPI and TOC are also close to those obtained using the same technoeconomic procedure and economic data [15, 17]. For the market price of products the internal rate of return is always above 20% for process concepts based on DME carbonylation. The largest rate of return was 28.74%, corresponding to the cases where methyl acetate, DME and power are produced (ATR-03 in Table 3). For the concepts based on DME hydrocarbonylation, the rate of return is lower, but still competitive if steam reforming or autothermal reforming is selected. The sensitivity analysis shows that the impact of uncertainties in TPI, TOC and market prices amounts to a maximum variation of +12/-10 points in the internal rate of return.

Despite the inherent complexity of a thermochemical biorefinery based on DME as an intermediate, similar profitability and energetic efficiency to other BTL/G processes producing a single product is achieved. Therefore, the concept analyzed is a promising route for biomass-derived fuels and chemical production.

Further work is needed to complement the analysis made in the present article, including: life cycle assessment, study of potential carbon footprint reduction, the possibility of extra revenue due to avoided greenhouse-gas (GHG) emissions, and optimization of the DME conversion reaction conditions at laboratory scale.

Acknowledgements

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Paper 6

Bio-syngas to gasoline and olefins via DME –
A comprehensive techno-economic assessment

This paper presents a technoeconomic assessment of a thermochemical biorefinery producing synthetic gasoline and ethylene and two BTL plants producing synthetic gasoline and olefins. All cases use DME as platform chemical and have been evaluated within the bioliq® project. It has been published as paper in 2013[*].

1. Introduction

The European Union enforces the use of biomass derived transportation fuels by setting a share of 10% biofuels for 2020 [1]. Synthetic gasoline produced from biomass is one of the most promising alternative fuels since it can be used in regular internal combustion engines without modifications. Furthermore biomass can reduce fossil CO_2 emissions by replacing non-renewable carbon sources in other applications, such as in the chemical industry. The bio-based production of olefins is a promising way to produce plastics from biomass. The integrated production of multiple products from biomass is currently discussed for future-expected thermochemical biorefineries using dimethyl ether (DME) as platform chemical, as for example using the DME (hydro)carbonylation route for the production of ethanol, methyl acetate DME and hydrogen from syngas (synthesis gas) [2]. In this study we assess the production of olefins and gasoline separately, i.e. two different concepts, and also the co-production (multiproduction) of gasoline and ethylene.

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[*] Haro P, Trippe F, Stahl R, Henrich E. Bio-syngas to gasoline and olefins via DME – A comprehensive techno-economic assessment. Appl Energy. 2013;108:54-65. DOI: 10.1016/j.apenergy.2013.03.015

Nomenclature

BTL: biomass-to-liquid
CC: combined cycle
DME: dimethyl ether
HHV: high heating value
IGCC: integrated gasification combined cycle
LPG: liquefied petroleum gas
MOGD: Mobil olefins-to-gasoline and distillate process
MTG: methanol-to-gasoline
MTO: methanol-to-olefins
PSA: pressure swing adsorption
RKS–BM: Redlich–Kwong–Soave with Boston–Mathias modifications
SRK: Soave–Redlich–Kwong
WWT: waste water treatment

The bioliq® concept, which is currently being developed at the Karlsruhe Institute of Technology (KIT) [3], allows the conversion of low-grade lignocellulosic biomass such as residual wood or straw to synthetic fuels and other chemicals, as illustrated in Figure 1. The bioliq® concept offers a two-stage approach to cope with the comparably low energy density of biomass. The first stage consists of multiple decentralized pyrolysis plants to liquefy the biomass collected from a radius of about 30 km around each pyrolysis plant. The slurry, which is a mixture of pyrolysis oil and char, offers a tenfold increased volumetric energy density and allows economical transportation over long distances to the centralized large scale gasification and synthesis plant [4]. The capacity of the gasification and synthesis plant should be as large as possible in order to profit from economies of scale and produce more efficiently and cost-effectively [5]. Pressurized entrained flow gasification is the technology currently best suited to process capacities of up to 1 GW of bio-slurry (thermal input) [4]. After cleaning and conditioning, the syngas can be used to synthesize fuels or chemicals by different pathways. The system boundaries of this study are limited to those of the synthesis section as shown in Figure 1. For the synthesis section, three concepts for gasoline, olefins and gasoline & ethylene production are designed. In earlier studies the authors assessed the pyrolysis step [6] as well as the production of syngas by entrained flow gasification [7]. The techno-economic assessment of the considered concepts is based on the results of the previous conversion steps of the bioliq® concept (pyrolysis and gasification).

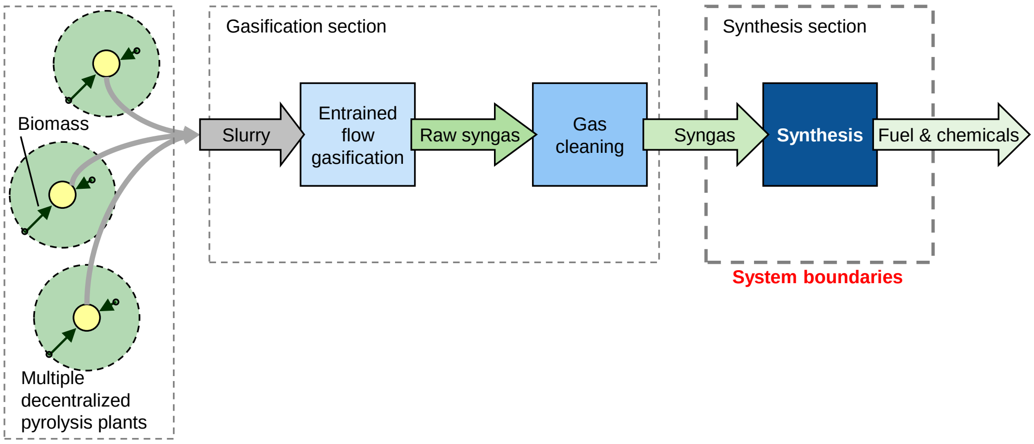

Figure 1. Overview of the bioliq® concept and system boundaries of this study.

The production of gasoline from coal or natural gas (through syngas) was a subject of interest during the 1980's due to the oil crisis. A few commercial plants were operated using the MTG (methanol-to-gasoline) technology or combining the MTO (methanol-to-olefins) and MOGD (Mobil olefins-to-gasoline and distillate process) technologies for gasoline production. These plants were shut down after the recovery of crude oil prices [8]. Currently, such processing is regaining attention but using biomass instead of coal as feedstock. A previous techno-economic assessment focusing on the conversion of coal into gasoline was carried out by Bridgwater et al. [9]. The study assessed the MTG and MTO-MOGD technologies, among others, technically and economically. Current studies are limited to the production of synthetic gasoline using biomass as feedstock [10-13]. Furthermore, the co-feeding of coal and natural gas in a plant producing synthetic gasoline has also been assessed [14]. The production of olefins from coal or natural gas (through syngas) was of less interest than the production of gasoline. The MTO technology, jointly developed with MTG, was implemented by Norsk Hydro in Norway using natural gas as feedstock [15]. However, there are currently several plants operating in China using coal as feedstock [16, 17]. The production of olefins from coal or natural gas instead of crude oil is a possible solution for the expected propylene gap, since (opposite to the refining of crude oil) the proportion of ethylene to propylene can be adjusted [18]. A previous study assessed the MTO process using lignocellulosic biomass as feedstock and demonstrated that the process could be cost-competitive at high crude oil price [18].

This study investigates the realization of the bioliq® concept converting clean and conditioned biomass-derived syngas in three different synthesis process alternatives (see Figure 1). The selected technologies in this assessment are currently available and have been demonstrated using coal or natural gas as feedstock. The whole plant is designed and assessed with realistic data and avoiding the assumption of future or expected (uncertain) developments. The biomass-derived syngas feed in all three concepts is first converted into DME. Different process conditions and catalysts in the DME conversion reactor lead to the production of gasoline or olefins. In the gasoline concept the main product is gasoline. Lighter hydrocarbons are used as fuel gas to generate electricity. Ethylene and propylene are the main products in the olefins concept. In this concept fuel gas is also used for electricity generation. The gasoline & ethylene concept combines the production of gasoline and olefins by using the olefins to gasoline process. Propylene and higher olefins are converted into gasoline whereas ethylene is recovered as product. For the considered concepts, two syngas feedstock options each are assessed which leads to six different cases.

Within the techno-economic assessment in this study the considered concepts are compared in terms of energetic efficiency and production costs. First the technology involved in converting syngas into gasoline and olefins and the respective process designs are presented. Following the methodology for the process modeling and techno-economic assessment is provided. The economic assumptions are based on a near future realization of the bioliq® concept in Germany. The results of mass and energy balances, investment estimation and production costs are outlined for each concept. The production costs of the respective products are compared to current market prices. Implications of CO_2 sequestration and mineral oil tax reductions on minimum product selling prices are discussed. Finally a sensitivity analysis for the economic results is conducted and conclusions of this study are drawn.

2. Process description and design

This section provides the definition of the input to the system boundaries in this study (synthesis section, see Figure 1), a summary of the technology involved in the main conversion steps and the process design for the considered synthesis concepts.

2.1. Syngas feed

The input for all considered concepts is the cleaned and conditioned syngas, with a molar H_2:CO ratio of 1, from the gasification section [7]. The syngas is fed to the synthesis plant at a temperature of 35 °C and with pressures of 35 or 75 bar for the 40 and 80 bar cases, respectively. The 40 and 80 bar cases represent two alternatives in the current technological development of the bioliq® process in the pilot plant in Karlsruhe and are therefore assessed in this study.

2.2. DME synthesis

Commercial processes for the production of DME from syngas are proven technology by companies like Haldor Topsoe A/S, Toyo Engineering Ltd., Air Liquide, S.A. or JFE Holding Inc. This study considers a single step reactor where methanol synthesis and in situ dehydration take place (commercial JFE's process [19]), as shown in the following equation:

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \qquad (1)$$

The advantage of the single step DME reactor is that syngas with an H_2:CO ratio of 1 – which is close to the natural composition of biomass-derived syngas – yields higher CO conversions than methanol synthesis. Data for process conditions of the DME synthesis reactor are shown in Table 1.

Table 1. Process conditions of the DME synthesis reactor (adapted from [20-22]).

Temperature (°C)		250
Pressure (bar)		35
CO conversion		0.85
Product distribution (% mass fractions)		
	DME	49.3
	MeOH	1.4
	CO_2	48.8
	H_2O	0.5

2.3. Gasoline and olefins synthesis and upgrading

Gasoline production from methanol was developed in the 1980s in response to the oil crisis. Several facilities were constructed but most of them were shut down when oil prices made the process unprofitable [23]. Such facilities could also use DME or mixtures of DME and methanol as feedstock [24]. Kinetics for the methanol and/or DME to gasoline conversion is described in [25]. Chang and Silvestri [25] found the dehydration of methanol to be the only difference between methanol and DME conversion without effect on the hydrocarbon distribution. The DME to hydrocarbon conversion is a complex reaction pattern of methylation, oligomerization, hydrocarbon formation and cracking using zeolites as catalyst [26]. The data for the process conditions of DME to gasoline reactors are shown in Table 2. The conversion of DME into gasoline results in about 22% light gases, 66% hydrocarbons in the light gasoline range and 12% on mass basis in the heavy gasoline range. The most prominent compound of the heavy gasoline fraction is durene (1,2,4,5-tetramethyl-benzene) which needs to be further processed in order to meet current gasoline specifications. The durene is isomerized to compounds with lower melting points in a fixed bed reactor in presence of hydrogen at 32 bar and 220 °C [10]. The upgraded heavy gasoline is blended with the light gasoline fraction to give total production of commercial grade gasoline.

The olefins production from methanol was developed along with gasoline production from methanol [23]. The reactor designs used in the gasoline production can also be used in the production of olefins. Differences can be found in catalysts and process conditions. In general, catalysts for the production of olefins are characterized by smaller pore sizes compared to production of gasoline [26]. Lower partial pressures of DME and higher reaction temperatures lead to a shift in the product distribution to lighter hydrocarbons [25]. Table 2 shows the main products ethylene and propylene make up about 84% on mass basis of total hydrocarbons produced.

A part of the olefins produced by the considered process can be converted into gasoline using similar catalysts as described by [30]. Olefins are fed to a fixed bed reactor operating at 30 bar and 340 °C and completely converted. This gasoline is advantageous compared to the above mentioned process in terms of gasoline quality, e.g. there is no significant durene content [25,26,30].

Table 2. Process conditions of DME to gasoline and DME to olefins reactors (are adapted from [10,11,18,25,27-29]).

		Gasoline	Olefins
Temperature (°C)		380	450
Pressure (bar)		33	4
DME conversion		1.0	1.0
Inert compounds (% v/v)	CO_2, CO, H_2, H_2O	66.5	39.1
Hydrocarbon distribution (% mass)			
	Ethylene	0.8	45.1
	Propylene	0.4	38.7
	Other light gases	18.2	7.9
	Butenes	2.5	8.3
	Light gasoline	66.3	-
	Heavy gasoline	11.8	-

2.4. Process design

Following, an overview of the process configurations selected for the techno-economic assessment of the synthesis section is provided taking the layouts from related references [8-11] as basis for the design. For each of the three considered concepts, the process from biomass-derived syngas to the respective final products is described.

The process flowchart of the gasoline concept is illustrated in Figure 2. In the 80 bar case the syngas is first expanded to meet the DME synthesis pressure of 35 bar. This brings an additional possibility in the 80 bar cases to generate electricity which is not available in the 40 bar case. Downstream of this point the 40 and 80 bar cases are identical. The syngas is led through the DME synthesis reactor and the whole outlet stream is heated up to 300 °C and sent to the gasoline synthesis reactor. The DME and gasoline synthesis reactors allow the generation of steam which is used for heat and power integration in the gasification and synthesis plant. The product stream of the gasoline synthesis reactor is degasified to remove unconverted syngas and CO_2 which make up about molar 60%. The required amount of hydrogen for the downstream isomerization reactor is recovered from the distillate stream in a pressure swing adsorption (PSA) unit. The bottom stream is led to a decanter where water is removed from liquid hydrocarbons. The recovered water is led to waste water treatment (WWT). Raw gasoline is split up into light and heavy fractions. Dissolved gases are removed from the light gasoline in a fractionation column. The heavy gasoline enters an isomerization reactor where durene is converted to a compound with lower melting point. The outlet stream is cooled and led to a gas-liquid-separator where hydrogen and light hydrocarbons are recovered. This and other fuel gas streams, shown in Figure 2, are fed to the gas turbine of the combined cycle to generate power. The waste heat of the gas turbine is used for high pressure steam generation. This is used in the steam turbine together with the steam generated by the gasoline synthesis reactor. The steam generated in the DME synthesis reactor serves for the thermal integration of the fractionation columns.

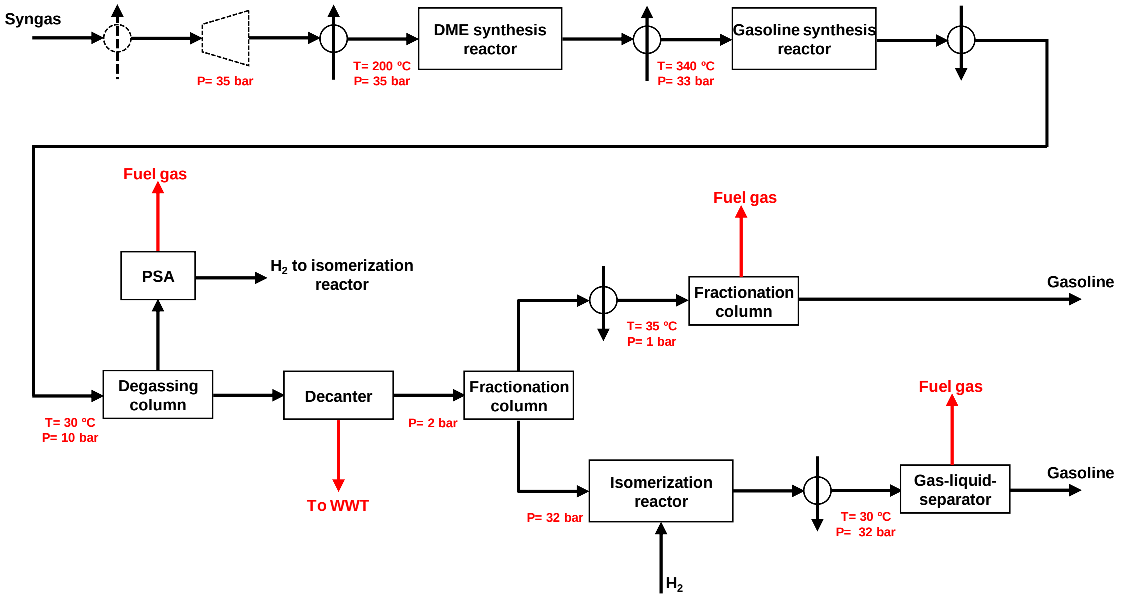

Figure 2. Process flowchart of the gasoline concept.

Figure 3 illustrates the process flowchart of the olefins concept. In analogues lines with the gasoline concept the expansion of the syngas in the 80 bar case is the only difference between the 40 and 80 bar cases. The outlet stream of the DME synthesis reactor is cooled before entering the first cryogenic fractionation column where unconverted syngas is removed. The separation of unconverted syngas from the product stream downstream of the olefins synthesis reactor would be less efficient. In order to meet the reaction conditions for the olefins synthesis, the pressure is decreased to 4 bar. The heat released in the olefins synthesis is used to reheat the reactor feed and to generate high pressure steam. Before entering the product recovery, the outlet stream of the gasoline synthesis reactor has to be recompressed and dewatered as well as CO_2 has to be removed. A Rectisol® unit operating at 39 bar [31,32] is used to separate the CO_2. The recovered CO_2 stream meets the requirements for subsequent transportation and sequestration. The downstream dewatering unit removes traces of water before entering the product recovery. First C_{2-} and C_{3+} hydrocarbons are split in a cryogenic fractionation column. The distillate stream is led to a cryogenic de-methanizer column where methane and traces of unconverted syngas are recovered. The bottom stream is fed to a cryogenic de-ethanizer column where ethylene and LPG (liquefied petroleum gas) are separated. The C_{3+} hydrocarbons enter a de-butanizer column where LPG, i.e. butenes, is recovered as bottom. The distillate goes into a de-propanizer column where propylene and LPG are separated.

Finally, total LPG contains about 60% butenes, 20% propane and 20% ethane on mass basis. The LPG product stream lowers the amount of fuel gas available for the gas turbine in the combined cycle. The waste heat of the gas turbine is also used for high pressure steam generation. This is used in the steam turbine together with the steam from the olefins synthesis reactor. The steam generated in the DME synthesis reactor is used for the thermal integration of the fractionation columns.

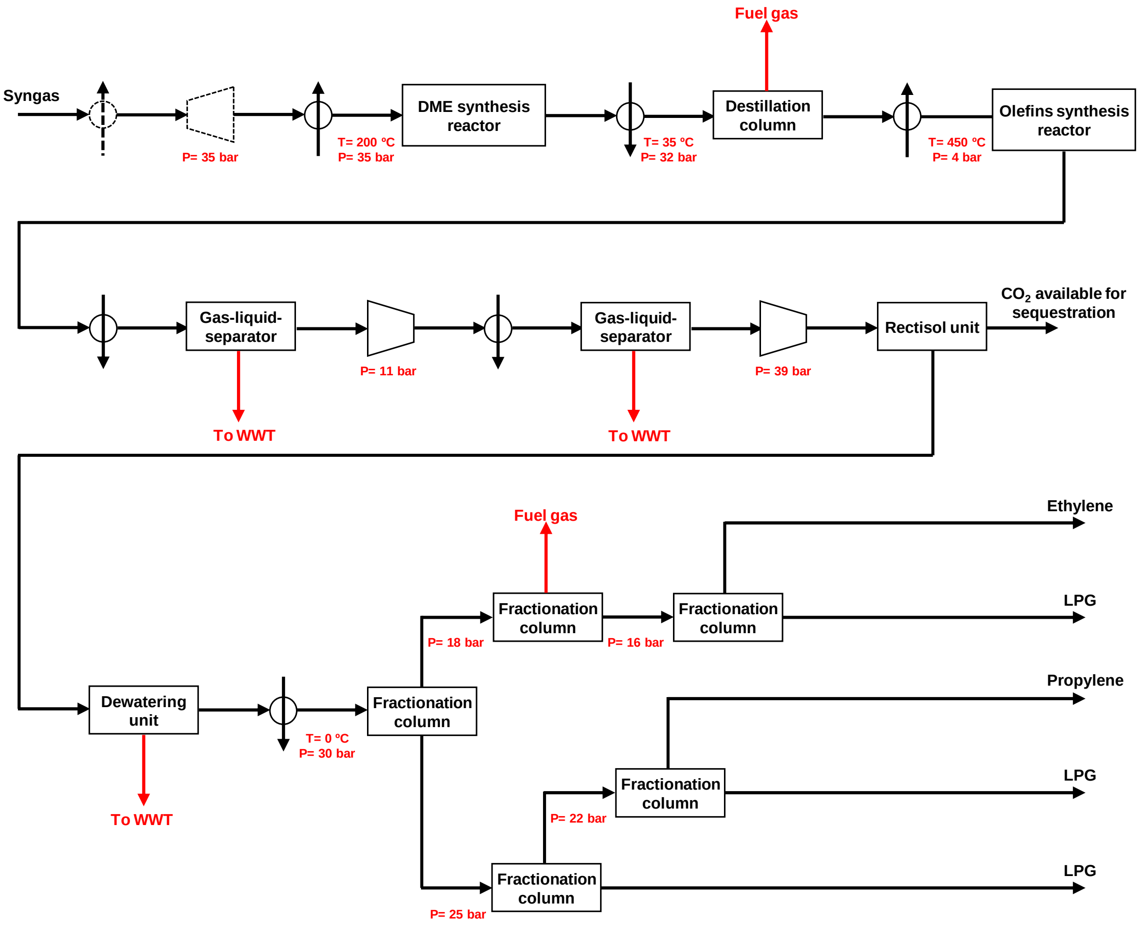

Figure 3. Process flowchart of the olefins concept.

As illustrated in Figure 4 the gasoline & ethylene concept is identical to the olefins concept except for the product recovery. In the gasoline & ethylene concept there is no LPG production and ethane recovered in the de-ethanizer column is used as fuel gas. The C_{3+} hydrocarbons are fed to the gasoline reactor. Since there is no water in the outlet stream of the gasoline reactor, only light hydrocarbon have to be removed. Because there is no LPG production the electricity generation in the combined cycle is increased compared to olefins concept.

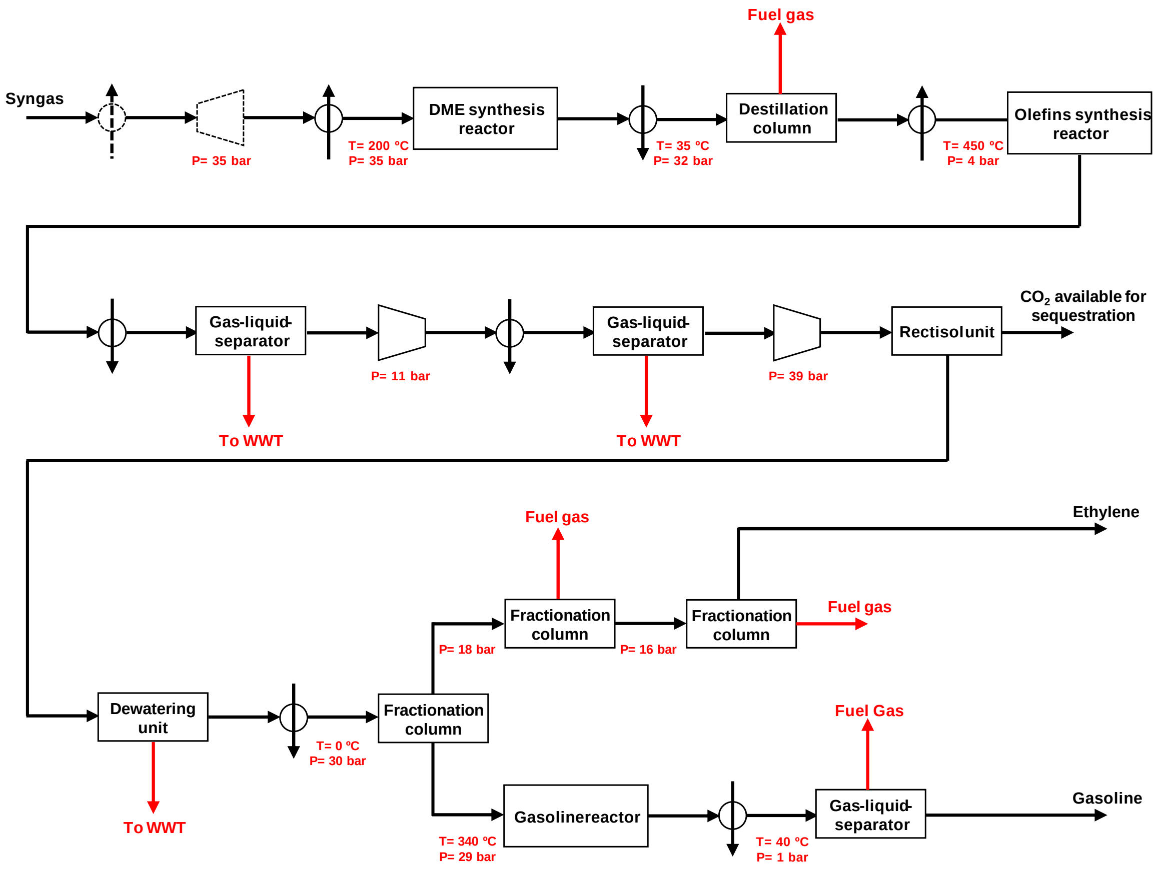

Figure 4. Process flowchart of the gasoline & ethylene concept.

3. Methodology

In order to conduct the techno-economic assessment for the considered gasoline and olefins production concepts, the mass and energy flows within the system boundaries are analyzed first. For this purpose, the process simulation software Aspen Plus is used. The mass and energy flow balancing builds up the foundation for the economic assessment. Fixed capital investment estimated for the respective equipment is derived using the determined capacities. Investment dependent costs together with personnel and other operating costs, as well as revenues from by-products, lead to specific production costs for the considered products in each concept. Finally, the robustness of the applied methodology is discussed.

3.1. Process modeling

Below, the most important criteria and assumptions used to simulate the considered concepts are outlined. The thermodynamic method used to model the high pressure processing is Soave–Redlich–Kwong (SRK). The low pressure processing is modeled using Redlich–Kwong–Soave with Boston-Mathias modifications (RKS–BM). These thermodynamic methods give accurate results in modeling hydrocarbon and light gases [33]. According to the experimental results of [21,22], an equilibrium reactor is used for the DME synthesis. The specific product yields of the DME to gasoline, DME to olefins and olefins to gasoline reactors are calculated in a spreadsheet using the distribution of hydrocarbons, according to Table 2, and fixing the remaining products to meet the atom balance. The isomerization of heavy gasoline is carried out in a RStoic reactor (stoichiometric reactor) where durene is assumed to be converted to 1,2,3,4-tetramethyl-benzene [10]. The modeling of synthesis reactors is summarized in Table 3.

Table 3. Reactor types used in Aspen Plus.

Process step	Type
DME synthesis reactor	REquil (equilibrium reactor)
Gasoline synthesis reactor	RYield (yield reactor)
Isomerization reactor	RStoic (stoichiometric reactor)
Olefins synthesis reactor	RYield (yield reactor)
Gasoline reactor	RYield (yield reactor)

Rigorous fractionation columns, i.e. RadFrac, are used to give accurate results in the product recovery. Column design and modeling in terms of molar split fractions, optimization of utility consumption and thermal integration of columns was performed according to [34]. Thermal integration of the considered concepts is carried out by using a minimum temperature difference of 20 °C for steam heating and generation as well as for water cooling. A minimum temperature difference of 40 °C is imposed for gas-to-gas heat transfer. An inventory of heat demand and supply is used to find the optimum thermal integration of each concept [2;35].

The process turbine and compressors as well as the gas and steam turbines in the combined cycle were modeled by assuming common isentropic and mechanical efficiencies [36] and according to Smith [34]. The gas turbine of the combined cycle is fed with high-pressure fuel gas streams, except in the case of gasoline concept, where the off-gas stream from the PSA unit needs to be compressed before entering the gas turbine. However, the overall efficiency of the combined cycle in this concept is still of 56%.

3.2. Economic assumptions

The economic assessment aims to determine gasoline and olefins production costs for six cases, i.e. three considered concepts and two syngas feed options each. To achieve this goal, the fixed capital investment for the considered concepts as described in the previous chapter is estimated. All equipment components are designed according to the mass and energy flows.

Investment data for the main equipment components are summarized in Table 4. Investment data for equipment components not listed in Table 4, e.g. heat exchanger and distillation columns, are calculated according to [38,39]. The investment data are converted into €, using the yearly average exchange rate of the respective year, and updated to the year 2010 [40]. To account for price developments of equipment components, the price index from Kölbel/Schulze [41] is used.

Based on the investment data for the main equipment components listed in Table 4, the total capital investment can be estimated using ratio factors for direct and indirect capital investment according to [38], as presented in Equation 2. Table 5 summarizes the assumed ratio factors for the control system, piping and further direct capital investments as well as the ratio factor for indirect capital investments, such as engineering or legal expenses. The ratio factors are selected according to process conditions, design complexity and required materials in this study. The applied ratio factor method implies uncertainties of ±30% [38].

The parameters presented in Table 6 used to calculate the investment dependent costs have also been used in the calculations for the pyrolysis plants and the gasification section. Further information about the methodology can be found in [6;7]. The syngas feedstock costs and prices, respectively, are adapted from previous studies by the authors and are based on biomass feedstock costs of 71 € per dry ton. The biomass feedstock costs include the transportation to the pyrolysis plants. If there is a net electricity surplus the revenue for electricity is supposed to be the same as the price in case of a net electricity demand. The stated price for hydrocarbon catalyst is applied for DME to gasoline, DME to olefins and olefins to gasoline catalysts.

Table 4. Summary of investment data for main equipment components (installed).

Description	Base scale	Unit	M€ 2010	Scaling Factor[a]	Reference
DME synthesis reactor	2.7	kmol of total feed/s	8.2	0.65	[37]
Gasoline synthesis reactor	1,347	kmol of DME/h	2.8	0.65	[11]
Olefins synthesis reactor	1,347	kmol of DME/h	6.0	0.72	adapted from [15]
Isomerization reactor	4,673	kg of heavy gasoline/h	1.8	0.70	[37]
Gasoline reactor	1,137	kmol of carbon feed/h	1.6	0.65	[11]
Hydrogen recovery unit	0.6	kmol of purge gas/s	4.0	0.74	[37]
Hydrogen compressor	0.7	MW_e	0.3	0.67	[37]
Rectisol® unit	44,141	Nm^3 of total feed/h	10.4	0.65	assumed
Cryogenic system	6.8	MW_{th}	6.0	0.70	[38]
Gas turbine	86.7	MW_e	12.1	0.75	[37]
Steam generator	317.0	MW_{th}	18.4	1.00	[37]
Steam cycle	141.0	MW_e	19.3	0.67	[37]

[a] The scaling factor (n) is used to scale the investment of the equipment from the base scale to the design scale, $\frac{Investment}{Investment_{base}} = \left(\frac{Design\ scale}{Base\ scale}\right)^n$.

Table 5. Ratio factors for direct and indirect capital investment (adapted from [38]).

Direct investments	*%*
Investment for installed equipment	100
Instrumentation and control	24
Piping	46
Electrical systems	8
Buildings	12
Yard improvements	7
Service facilities	48
Total direct investment	**245**
Indirect investments	*%*
Engineering and supervision	22
Construction expenses	28
Legal expenses	3
Contractor's fee	15
Contingency	30
Total indirect investment	**98**
Fixed Capital Investment	**343**

$$Fixed\ capital\ investment = I_{IE} \cdot [1 + \sum_{i=1}^{n} f_i] \qquad (2)$$

I_{IE} Investment for installed main equipment components

f_i Ratio factor for direct/indirect capital investment i = 1...n

Table 6. Summary of economic assumptions.

Parameters for investment dependent costs		
Capacity factor	%	80
Expected lifetime	Years	20
Depreciation (no scrap value)	linear	-
Interest rate	%	7.0
Working capital	% of fixed capital investment	5.0
Maintenance costs (average)	% of fixed capital investment	3.0 – 3.6
Insurance & taxes	% of fixed capital investment	2.0
Prices for consumables		
Syngas 40 bar (adapted from [7])	€/Nm^3	0.243
Syngas 80 bar (adapted from [7])[a]	€/Nm^3	0.238
Electricity [42]	€/MWh	99.3
Cooling water [11]	€/m^3	0.26
Waste water treatment [7]	€/m^3	0.32
DME catalyst costs [10]	€/kg	22
Hydrocarbon catalyst [10]	€/kg	113
Market prices of products (without taxes)		
Gasoline (2011 average, [43])	€/L	0.651
Ethylene (2011 average, [44])	€/t	1,140
Propylene (2011 average, [44])	€/t	1,120
LPG (assumed by authors)	€/kg	0.980

[a] The syngas with 80 bar pressure can be produced at lower costs because the efficiency of the entrained flow gasifier is higher at 80 bar (see [7] for details).

4. Results

The following section summarizes the resulting mass and energy balances as well as fixed capital and production costs estimations. The results for the six cases are listed. They comprise two kinds of syngas input for the gasoline, olefins and gasoline & ethylene production concepts. The different pressure levels of syngas are due to the respective operating pressure in the entrained flow gasifier. However, there is only one pressure level in the considered hydrocarbon synthesis options. The most prominent consequence is an additional electricity generation possibility in the 80 bar cases.

4.1. Mass and energy balances

Table 7 illustrates the mass and energy balances for the gasoline, olefins and gasoline & ethylene production from biomass-derived syngas. In all considered processes the syngas input is identical in terms of mass flow and HHV (higher heating value) content. In the gasoline production concept the difference between the 40 and 80 bar cases is the generation of about 5 MW additional electricity which is the consequence of the higher pressure in the syngas input. This is also applicable for the olefins and gasoline & ethylene production concept, since the DME synthesis is always operated at same conditions. Compared to the gasoline concept, the total hydrocarbon production in the olefins and the gasoline & ethylene concepts is 23% and 16% higher. On the opposite side, the gasoline concept leads to the highest electricity generation by converting a higher amount of fuel gas in the combined cycle. The electricity generation in the olefins and gasoline & ethylene concept is about 70% and 57% lower. However, the net electricity generation stated in Table 7 is only referring to the generation and consumption within the synthesis section (system boundaries of this study). The global electricity balance, also shown in Table 7, includes the pyrolysis plants and gasification section.

$$Energy\ efficiency = \frac{products\ (MW_{th})}{biomass\ (MW_{th}) + \frac{net\ electricity}{\eta_e}(MW_{th})} \qquad (3)$$

In order to make a fair comparison of all concepts the total energy efficiency from biomass to final products is also shown. The additional upstream electricity consumption in the pyrolysis plants as well as the gasification and gas cleaning accounts for 68 and 66 MW in the 40 and 80 bar case, respectively. This leads to an additional electricity input in the olefins and gasoline & ethylene production. The additional electricity input is converted to an HHV equivalent by assuming conversion efficiency (biomass to electricity) of 39% (typical for an IGCC plant using biomass). The total energy efficiency calculated according to Eq. (3) ranges between 37.5% and 41.1% corresponding to the gasoline and the olefins concepts. The gasoline & ethylene concept lies in between the other concepts, but is closer to the gasoline concept. In terms of energy efficiency the olefins concept prevail over the other concepts. Increased hydrocarbon production leads to higher efficiencies. Furthermore the specific HHV on mass basis of olefins compared to the average of gasoline is about 5% higher. Regarding the whole bioliq® plant the energy losses of the gasoline concept are described in Figure 5, where the energy content of biomass is expressed on HHV basis. Major efficiency losses occur before the synthesis section, i.e. the pyrolysis of biomass reduces the energy content by about 15% and the gasification has an efficiency of about 78%.

Table 7. Mass and energy balances for the considered process concepts.

	Gasoline		**Olefins**		**Gasoline & Ethylene**	
	40 bar	80 bar	40 bar	80 bar	40 bar	80 bar
Input to system boundaries						
Syngas in t/h (MW HHV)	144 (760)	144 (760)	144 (760)	144 (760)	144 (760)	144 (760)
Output from system boundaries						
Gasoline in t/h (MW HHV)	30.0 (394)	30.0 (394)	-	-	18.2 (239)	18.2 (239)
Ethylene in t/h (MW HHV)	-	-	16.6 (230)	16.6 (230)	16.6 (230)	16.6 (230)
Propylene in t/h (MW HHV)	-	-	14.3 (199)	14.3 (199)	-	-
LPG in t/h (MW HHV)	-	-	6.0 (84)	6.0 (84)	-	-
Electricity generation in MW net (gross)	117 (123)	123 (128)	34 (55)	39 (60)	49 (70)	54 (75)
Electricity balance in MW[a]	-49	-57	34	27	19	12
Energy efficiency in % (HHV basis)						
From syngas to products[b]	67.2	68.0	72.0	72.6	68.1	68.8
From biomass to products[c]	37.5	38.2	40.5	41.1	38.1	38.7

[a] Refers to the global electricity balance of the whole bioliq® concept, including the pyrolysis plants and the gasification and synthesis plant. A positive value indicates that electricity is imported.

[b] The energy efficiency from syngas to products refers to the efficiency of the synthesis plant assessed in this study.

$$Energy\ efficiency = \frac{products\ (MW_{th}) + output\ electricity\ (MW_e)}{syngas\ (MW_{th}) + \frac{input\ electricity}{\eta_e}(MW_{th})}.$$

[c] The energy efficiency from biomass to final products is calculated using Eq. (3).

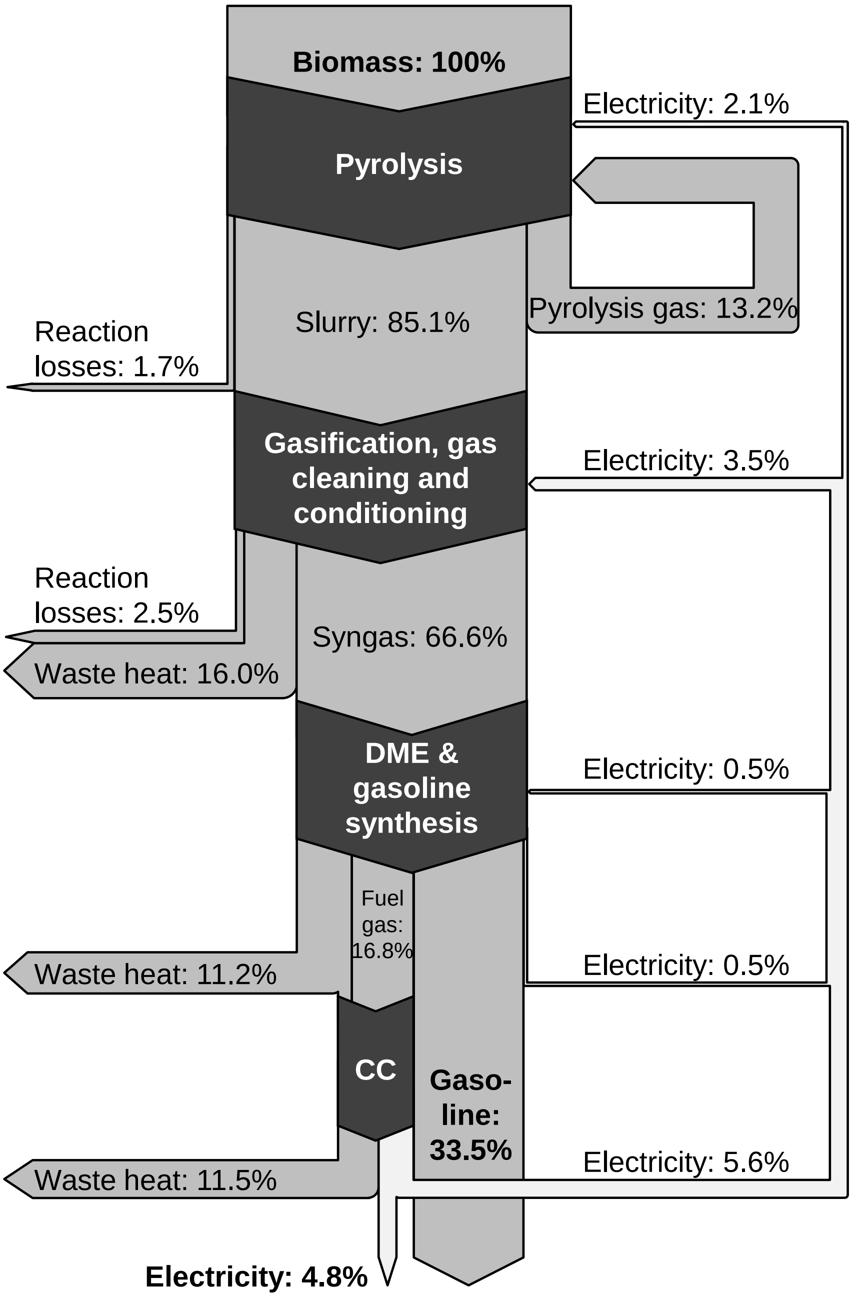

Figure 5. The Sankey diagram of the whole bioliq® plant for the gasoline concept (80 bar). CC: combined cycle.

4.2. Economic evaluation

Figure 6 shows the fixed capital investment corresponding to the system boundaries of this study. Comparing the 40 and 80 bar cases within the different production concepts, the increase in fixed capital investment is mainly caused by the additional process turbine. The gasoline concept requires the lowest investment. The synthesis and product recovery make up about half of the fixed capital investment, the other half belongs to the power island. The investment for synthesis and product recovery in the olefins concept is twice as high, but the power island accounts for only half compared to the gasoline concept. This is mostly due to the more capital intensive product recovery and additional equipment in between the synthesis steps as shown in Figure 3. The investment for the gasoline & ethylene concept is close to the olefins concept, since the process design is the same, but the propylene recovery which is replaced by the olefins to hydrocarbon synthesis. The realization of the whole bioliq® concept including entrained flow gasification, gas conditioning and cleaning as well as about 10 decentralized pyrolysis plants with 100 MW_{th} capacity to meet the slurry consumption of the gasification and synthesis plant is adding 930 and 890 M€ for the 40 and 80 bar cases, respectively, to the above mentioned fixed capital investment.

The specific production costs for the considered concepts are presented in Figure 7. The production costs are indicated in € per kg of hydrocarbon to help the comparison of respective products. Due to the system boundaries in this study the syngas costs include the total upstream operating costs. For this reason there are electricity revenues in all cases regardless of total net electricity generation or consumption in each case (see also Table 7). The syngas costs are by far the largest contributor to the production costs. The final specific production costs of hydrocarbons from biomass in the gasoline concept are the lowest. The sum of the production costs (excluding revenues) in the gasoline concept is close to the olefins concept, but the revenues for excess electricity lead to a difference of 0.08 € per kg of hydrocarbons. In the olefins case the hydrocarbon products are ethylene and propylene. The lower electricity revenues in the olefins concept are only partly compensated by LPG revenues. In the gasoline & ethylene concept the specific syngas costs are lower, but this is due to the higher hydrocarbon production. This is also applicable to the other operating cost components in analogue lines.

For the calculation of specific production costs in Table 8 the prices of by-products, i.e. electricity and LPG, are fixed (see Table 6). For the gasoline concept the specific production costs are 77% and 72% higher than the current market price (shown in their common units: per litter and per GJ). For the olefins concept the difference to the current market prices of ethylene and propylene is reduced to 44% and 40%. The specific production costs in the gasoline & ethylene concept are 63% and 59% higher than current market prices. For the calculation in the concepts with two main products, we assume that the relation between specific production costs remains the same as in the current market prices. Considering mineral oil taxes in Germany the selling price for gasoline is not about 0.651 €/L, but 1.306 €/L ([43]). To be competitive to fossil gasoline, tax reductions for biomass-derived gasoline could be a solution. This is discussed in the next section.

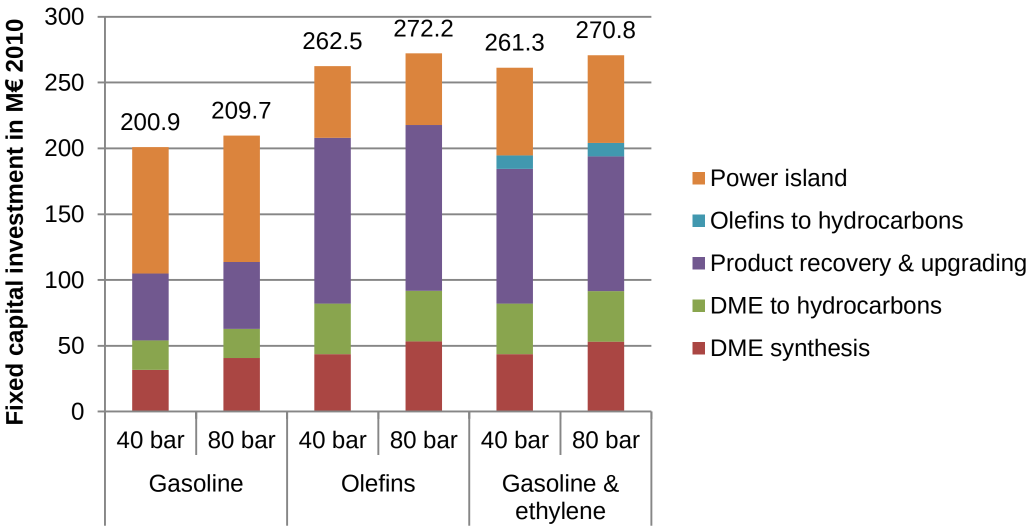

Figure 6. Fixed capital investment for the considered process concepts.

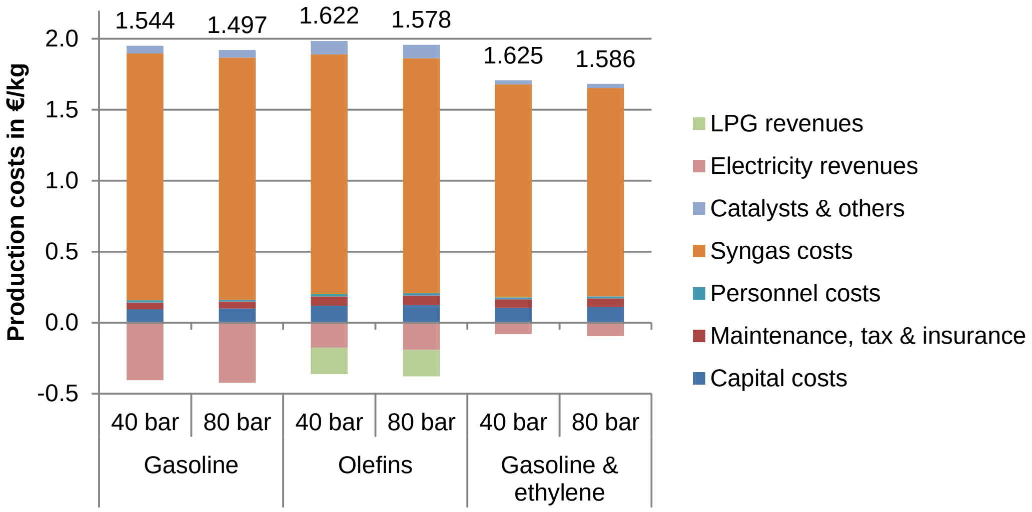

Figure 7. Specific production costs on mass basis.

Table 8. Specific production costs for main products in the considered concepts.

	Gasoline		Olefins		Gasoline & Ethylene	
	40 bar	80 bar	40 bar	80 bar	40 bar	80 bar
Gasoline in €/L	1.154	1.119	-	-	1.059	1.034
Gasoline in €/GJ	41.25	40.64	-	-	37.32	36.80
Ethylene in €/t	-	-	1,635	1,591	1,853	1,809
Propylene in €/t	-	-	1,607	1,563	-	-

5. Implications of CO_2 sequestration and mineral oil tax reductions

As described in the economic results the specific production costs for gasoline and olefins produced from biomass are currently not competitive. In the before mentioned process designs there is CO_2 available for sequestration. Since all the CO_2 available for sequestration comes from biomass which is neutral in climate change regulations, the effect of the CO_2 sequestration can be translated into avoided emissions. These avoided emissions have not been regulated yet. For the following assessment, the authors assume that there is the possibility to sell these avoided emissions via CO_2 certificates.

In the following analyses only the more promising 80 bar cases presented in Chapter 4.2 are evaluated. The CO_2 emissions due to the pyrolysis, gasification and synthesis steps are similar for all concepts, as presented in Table 9. The higher emissions in the gasoline and gasoline & ethylene concepts result from lower hydrocarbon production. There is CO_2 available for sequestration in the gas cleaning section of all concepts. In the olefins and gasoline & ethylene concepts there is additional CO_2 available in the synthesis section (the system boundaries of the study).

In order to meet technical specifications for transport and sequestration, the CO_2 removed from the process has only to be compressed (see 2.3). The authors assume that a pressure of 100 bar is sufficient for transportation and subsequent sequestration [45]. Additional capital and operating costs are caused by the compressors which amount to 20 € per t of CO_2. Including transportation and sequestration, the total CO_2 mitigation costs amount to 39 € per t of CO_2. This leads to the conclusion that CO_2 would be sequestrated for prices of CO_2 certificate higher than 39 €/t.

Table 9. Summary of CO_2 emissions, sequestration and mitigation costs.

		Gasoline	**Olefins**	**Gasoline & Ethylene**
CO_2 emissions from biomass conversion	*TOTAL*	319.2	295.7	302.7
	Pyrolysis[a]	89.9	89.9	89.9
	Gasification[a]	101.5	101.5	101.5
	Synthesis	127.8	104.3	111.3
CO_2 available for sequestration in t/h	*TOTAL*	88.0	125.3	125.3
	Gasification[a]	88.0	88.0	88.0
	Synthesis	0	37.4	37.4
CO_2 transportation costs in €/t	[45]	4		
CO_2 sequestration costs in €/t	[45]	14		
Total CO_2 mitigation costs in €/t		39		

[a] Outside of system boundaries in this study.

Figure 8 compares the possibilities of subsidies for the considered products from industry via CO_2 certificates and from public sector via mineral oil tax reductions. Using CO_2 certificates to make the considered products profitable leads to 150 €/t in the olefins concept, 202 €/t in the gasoline & ethylene concept and up to 252 €/t in the gasoline concept. The IEA (International Energy Agency) considers prices of up to 200 €/t for CO_2 certificates in Europe in 2040 ([45]). In the gasoline concept there is no longer an effect of CO_2 certificates prices as soon as it drops below 39 €/t.

Since the prices for CO_2 certificates are far from current market prices, mineral oil tax reductions are another option to strengthen the competitiveness in the medium term. Of course, the tax reductions would only have an impact on gasoline. In order to meet the current market price for gasoline a mineral oil tax reduction of 71% would be required. Even a tax reduction of 100% would not be enough to make the gasoline & ethylene concept competitive. There is no impact of tax reduction in the olefins concept.

Evaluating the ranking of the considered concepts, three areas can be distinguished in Figure 8. In case of mineral oil tax reductions of less than 30% the olefins concept would be most promising. For mineral oil tax reductions of more than 40% the gasoline concept would be first to become competitive. If mineral oil tax reductions range between 30% and 40%, the difference between the respective concepts is not significant.

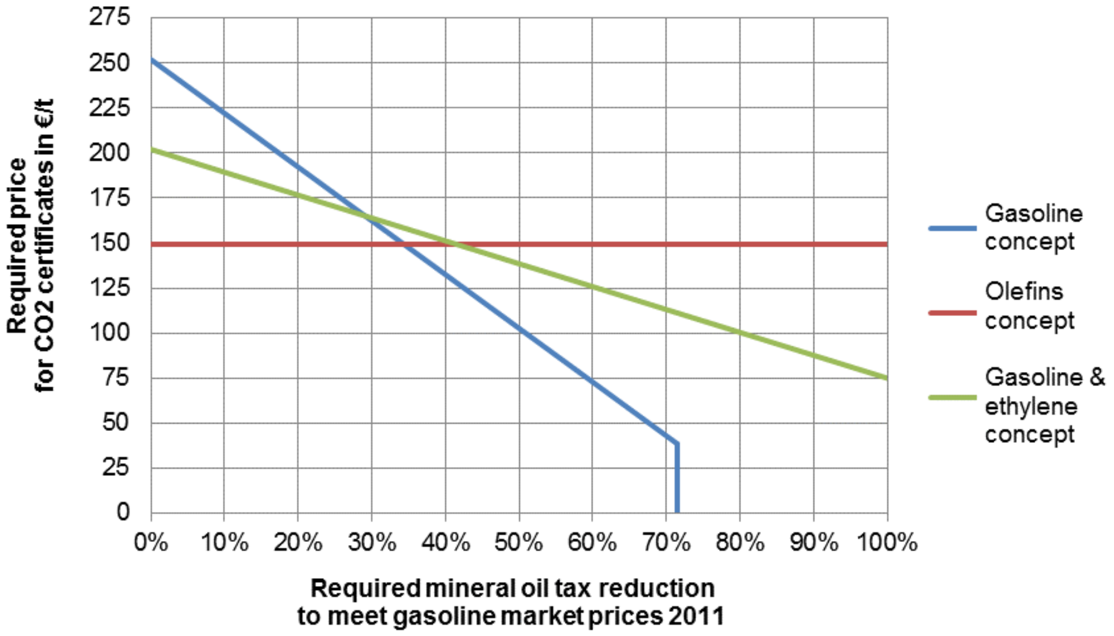

Figure 8. Required subsidies through CO_2 certificates versus mineral oil tax reductions.

6. Discussion and sensitivity analysis

The before mentioned results of this study show that the production of gasoline and olefins from biomass is not competitive at current market prices. However, this is not a result of the technology involved, but of the assumed biomass feedstock costs. To demonstrate the competitiveness of the technologies scenarios with 90% coal and 10% biomass-derived slurry on energy basis as input in the gasification are analyzed. The coal price used in the calculation is 107 €/t which corresponds to the yearly average of 2011 in Germany ([42]). The specific production costs of gasoline are 0.663 and 0,691 €/L in the gasoline and gasoline & ethylene concepts, respectively. The specific production costs of ethylene are 996 and 1,208 €/t in the olefins and gasoline & ethylene concepts, respectively. All the calculated prices in this scenario are very close to the current market prices, so the technology is competitive to conventional refinery processes. These results are in agreement with the recent interest of some companies in the construction of new MTO and MTG plants using coal [16,17]. Except for the coal fed, the calculation of these specific production costs is conducted with the same assumptions as for the results presented in Table 8. In comparison to related studies for the production of gasoline from biomass through syngas [10,11,13], the process layout and efficiencies are similar (except the efficiency for [13] which is larger). The production costs of this study are twice the values of references [11,13] and slightly above to those of reference [9]. The main reason for the discrepancies with previous assessment relies on the different assumptions of each study. Whereas in these related studies, assumptions of expected improvements have been made for the gasification [13], conversion technologies [11,13] or feedstock cost ([11] uses 56 US$ per dry tonne versus 71 € per dry tonne of this study); this study is focused on the realization of the bioliq® concept using technical data from the plant in Karlsruhe and only currently commercial technologies with realistic assumptions. Hence, this study achieves the highest production costs of all the studies from the literature of synthetic gasoline production. In case of olefins production there is only one reference and the results are similar to those presented here [18].

The reduction of mineral oil taxes and the selling of CO_2 credits are potential subsidies to support the process' profitability. Looking for a medium term scenario, where the expected improvement in gasification and syngas conversion technologies are not available, the sought of extra revenues must be accomplished. The reduction of mineral oil taxes is a known option, already in use in some countries to enhance the production and consumption of biofuels. The possibility of CO_2 storage and sequestration in the assessed plants (pre-combustion) has a better economy than in regular power plants (post-combustion) and, due to the neutral origin of the carbon, can be sold as CO_2 credits (emissions trading).

An important contribution of this study is the combination of two different but related BTL (biomass-to-liquid) processes for the production of gasoline and ethylene from biomass-derived syngas. This design of a thermochemical biorefinery, i.e. a thermochemical processing plant with multiproduction of gasoline and ethylene is firstly proposed. Benefits of thermochemical biorefineries are still on discussion, but they bring a better position for market fluctuations, since the production is diverted into different sectors (energy and petrochemicals).

The effect of the biomass feedstock price on the specific production cost of gasoline is illustrated in Figure 9. As mentioned before the biomass feedstock costs also include the transportation costs to the pyrolysis plants. A doubling of biomass feedstock costs results in a 38% increase in the specific production cost of gasoline. Figure 10 shows the effect on the olefins concept. Since there are two main products in this case, the weighted average of ethylene and propylene specific production costs is calculated. A doubling of biomass feedstock costs in this concept leads to a 35% increase in the specific production cost of olefins.

As mention in the methodology, the fixed capital investment method has an accuracy of ±30%. To evaluate the sensitivity of specific production costs to the total fixed capital investment, the conservative deviation of +30% is calculated for the gasoline and olefins concepts. In order to make a fair analysis the fixed capital investment of the pyrolysis and gasification steps are also included. In the gasoline concept an increase of 30% in total fixed capital investment results in a 16.5% higher specific production cost. In the olefins concept this increase leads to 16.1% higher specific production cost. The high sensitivity to changes in the fixed capital investment emphasizes the importance of profiting from economies of scale as intended by the bioliq® concept.

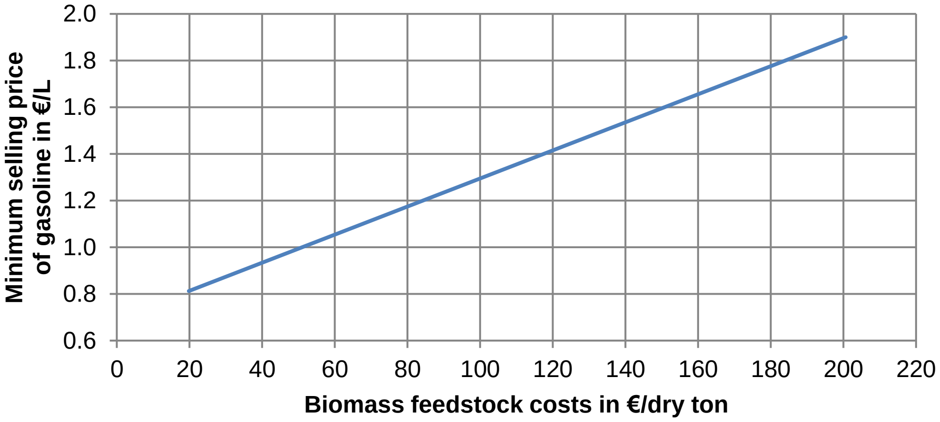

Figure 9. Sensitivity of gasoline specific production cost to biomass feedstock cost.

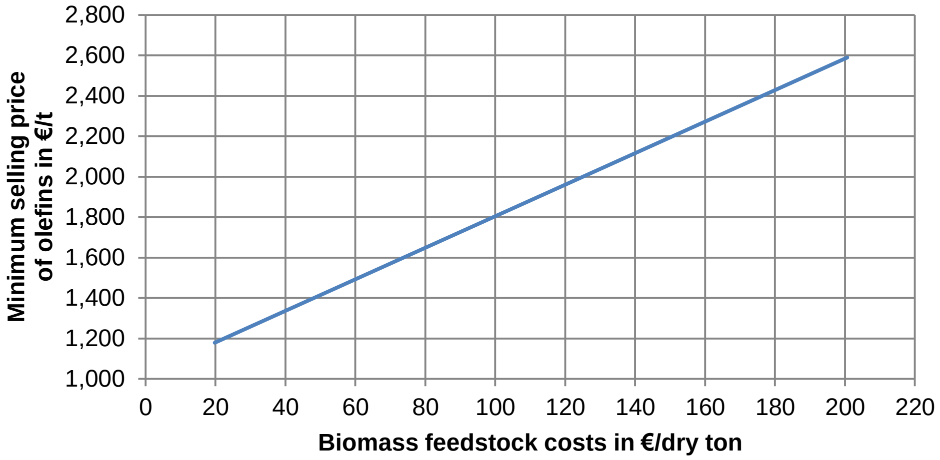

Figure 10. Sensitivity of average ethylene and propylene specific production cost to biomass feedstock cost.

7. Conclusions

A comparative techno-economic assessment for the realization of the bioliq® concept for the production of gasoline, olefins and gasoline & ethylene is performed. The three considered concepts use DME as a platform chemical. Previously to this study, the pyrolysis and gasification steps were designed and assessed with realistic data (from the bioliq® plant in Karlsruhe). These assessments build up the basis for the assessment of the synthesis section. The three different synthesis concepts described in this study are modeled using commercial technologies for the conversion of DME using coal and natural gas. The combination of two different, but related, BTL processes for the production of gasoline and olefins is proposed as an example of the design of a thermochemical biorefinery. This concept (gasoline & ethylene) achieves the multiproduction without penalization of economics or efficiency with respect to the case of single gasoline and olefins production.

The total energy efficiency ranges between 37.5% and 41.1% corresponding to the gasoline and the olefins concepts. Resulting specific production costs in the gasoline concept are 77% and 72% higher than the current market price for the 40 and 80 bar cases, respectively. For the olefins concept the difference to the current market prices of ethylene and propylene is reduced to 44% and 40%. The specific production costs in the gasoline & ethylene concept are 63% and 59% higher than current market prices. This is not a result of the technologies involved, but of the biomass feedstock costs. The possibility to sequestrate CO_2 within the considered concepts at costs of about 39 €/t allow additional revenues from CO_2 sequestration. This possibility is analyzed for the more promising 80 bar cases. In order to make the considered products profitable, CO_2 certificate prices of 150 €/t in the olefins concept, 202 €/t in the gasoline & ethylene concept and up to 252 €/t in the gasoline concept would be required. The reduction of mineral oil tax is also considered. To meet the current market price for gasoline with only tax reduction, a reduction of 71% would be necessary in the gasoline concept. The combination of both kinds of subsidies is also evaluated in this study.

The results of the assessment show that the production costs of the considered products are far from current market prices, which prevents potential investors from using biomass. Process development in order to achieve higher efficiencies or simpler process designs with lower capital requirements are one way towards competitiveness. Nevertheless, the results also point out that the public sector might enhance the competitiveness by implementing subsidies and/or regulation on CO_2 emissions.

Acknowledgements

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Paper 7

A proposal of methodology for the assessment of sustainability in thermochemical biorefineries: Application to thermochemical biorefineries based on dimethyl ether as a platform chemical

This paper proposes a methodology for the assessment of environmental sustainability in thermochemical biorefineries focused on multiproduction. The proposed methodology is used for the assessment of the case studies of Paper 5[*]*.*

1. Introduction

The certification of sustainability in biorefineries is based on a life cycle assessment of GHG emissions using a specific methodology, which is regulated by governments and international organizations. The consecution of the sustainability would allow the biorefinery to achieve different benefits from the use of renewable feedstocks (task reductions or exceptions, regulated market, subsidies, etc.). However, regulation in the EU focuses on current technologies for biomass valorization into transportation fuels (energy-driven biorefineries). Biorefineries focused on multiproduction (co-production of transportation fuels, other fuels, chemicals, electricity and heat) are considered only marginally and chemicals are excluded in the calculation of the potential saving of GHG emissions.

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[*] Haro P, Aracil C, Vidal-Barrero F, Ollero P. Manuscript.

Nomenclature

BECCS: bioenergy with carbon capture and storage

CCS: carbon capture and storage

DME: dimethyl ether

E: total emissions from the use of the fuel

E': total emissions until the biorefinery (cradle to gate)

e_{ccr}: emissions saving from carbon capture and replacement

e_{ccs}: emissions saving from carbon capture and geological storage

e_{ec}: emissions from the extraction or cultivation of raw materials

e_{ee}: emissions saving from excess electricity from cogeneration

E_{Fi}: emissions from the fossil fuel comparator

E_i: emissions of the co-product/service i (cradle to grave)

e_l: annualized emissions from carbon stock changes caused by land-use change

E_m: total emissions (multiproduction plants) from the use of all co-products (services included)

e_p: emissions from processing

e_{sca}: emissions saving from soil carbon accumulation via improved agricultural management

e_{td}: emissions from transport and distribution

e_u: emissions from the final use

GHG: greenhouse gas

GWP: global warming potential

IRR: internal rate of return

LCA: life cycle assessment

LHV: low heating value

SOC: soil organic carbon

VOC: volatile organic compounds

x_i = allocation factor for the co-product/service i

The present study proposes a methodology (based on European regulation) for thermochemical biorefineries with multiproduction, integrating the allocation of different kinds of co-products (never assessed to date) and electricity. In addition, the final use of products is further investigated, since it is crucial in the sustainability assessment of plants producing chemicals. The incorporation of BECCS (BioEnergy with Carbon Capture and Storage) is also discussed. The incorporation of CCS technologies in plants processing biomass is of recent interest and it is recognized as an option in European regulation. However, literature in the field is scarce. If sustainability is easily achieved and there is an extra saving of GHG emissions, the extra-avoided emissions could be translated into an economic benefit. A first alternative is the co-feeding of fossil fuels in the biorefinery to reach the minimum reduction of GHG emissions in order to achieve sustainability. The second alternative considered in this paper is the sale of the extra-avoided emissions, via CO_2 credits (emission trading).

In a previous publication, a set of 12 different concepts of a thermochemical biorefinery using DME as a platform chemical was presented and technoeconomically assessed [1]. The conclusions of this study were highly satisfactory, although the assessment of sustainability was not included. The proposed methodology in this paper is used for the assessment of the sustainability of these concepts of a thermochemical biorefinery, which have been modified for the incorporation of BECCS. The final use of each co-product and the possibility of valorization of the resulting extra-avoided emissions are discussed and economically assessed.

2. Methodology

The methodology used in this study refers when possible to that presented in Directive 2009/28/EC of the European Parliament and Council [2]. The common calculations are briefly commented upon and further details can be found in the Directive. Those calculations that are new or extended with respect to the Directive are commented upon in detail. This study refers to a cradle to grave assessment and the functional unit is MJ of total products and services per year.

The Directive gives a general formula for the calculation of GHG emissions of biofuels and bioliquids:

$$E = e_{ec} + e_{l} + e_{p} + e_{td} + e_{u} – e_{sca} – e_{ccs} – e_{ccr} – e_{ee} \text{ (g } CO_2 \text{ equivalent / MJ of biofuel)}$$

This formula does not consider chemicals as potential products. In order to do so and to include the possibility of multiproduction, a different (but equivalent) version is used:

$$E_m = E' + \text{sum}[x_i \cdot (e_{td,i} + e_{u,i})] \text{ (g } CO_2 \text{ equivalent / MJ of all co-products and services)}$$

$$E' = e_{ec} + e_{l} + e_{p} - e_{sca} – e_{ccs} – e_{ccr}$$

$$E_i = x_i \cdot E' + e_{td,i} + e_{u,i} \text{ (g } CO_2 \text{ equivalent / MJ of i)}$$

The saving of GHG emissions should also be modified for the inclusion of multiproduction, since there is a different fossil reference for each co-product and service (electricity). Then, an individual saving could be calculated for each co-product, the global saving being the weighted average:

$$\text{Saving}_i = (E_{Fi} – E_i)/E_{Fi}$$

$$\text{Saving} = \text{sum}(x_i \cdot \text{Saving}_I)$$

If there is an extra saving (regarding the minimum 60% commitment by the EU for 2018 [2]), it is calculated using the following expression:

$$\text{Extra saving} = \text{sum}(x_i \cdot E_{Fi}) \cdot 60\% - E_m \text{ (g } CO_2 \text{ eq/MJ of all co-products and services)}$$

The extra saving can be translated into an economic benefit in different ways. In this study only two options are analyzed: (1) via CO_2 credits (emission trading), and (2) via co-feeding of a fossil fuel. The equivalent amount of CO_2 that is saved above the limit regulated is an extra-avoided emission[†], which could be sold in the emission trading. The co-feeding of coal (or other

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[†] It is assumed that a reduction of GHG emissions larger than that required could be used for the enhancement of the profitability via the sale of CO_2 credits (emissions trading). The avoided emissions include the potential negative emissions (net outlet of equivalent CO_2 from the atmosphere).

fossil fuels) will reduce the saving by introducing non-biogenic carbon into the biorefinery; the amount to reach the limit set by regulation is the maximum amount of coal that can be co-fed in order to mantain sustainability.

$$\text{Extra-avoided emissions (g } CO_2 \text{ eq/s)} = \text{Extra saving} \cdot \text{Total production (MW)}$$

$$\text{Co-feeding of coal } (MW_{th}) = \text{Extra saving} / (E_{F,coal} + \text{Extra saving} / \text{Plant capacity})$$

2.1. Calculation of E’

For the calculation of E’ it is assumed that an energy crop is used as feedstock.

In the case of thermochemical biorefineries, the value for e_{ec} could correspond to the value for farmed wood for DME synthesis (Annex 5 of the Directive, [2]).

The value of e_l depends on the region, the kind of soil and the previous use of the land. However, emissions associated with indirect changes in land-use are currently not included[‡], since they are not yet regulated.

In this study, 3 different cases have been considered in order to give a view of the qualitative differences regarding the direct land-use change, all of them supposing that the location of the land will be in a Mediterranean country. However, the case of no land-use change has been preferred as the neutral case for further discussion of the results.

The Directive provides a formula to calculate annualized emissions from carbon stock changes due to land-use change:

$$e_l = (CS_R - CS_A) \cdot 3{,}664 \cdot 1/20 \cdot 1/P - e_B$$

The values of CS_R y CS_A are obtained from the Commission Decision of 10 June 2010 [3]. This Decision provides a formula to determine the soil organic carbon stock:

$$CS_i = (SOC + C_{VEG}) \times A \quad \text{where} \quad SOC = SOC_{ST} \times F_{LU} \times F_{MG} \times F_I$$

In this study, the values of SOC_{ST}, F_{LU}, F_{MG}, F_I Y C_{VEG} are taken from the guidelines provided for mineral soils in the Decision.

The value of e_p is determined by the configuration of the biorefinery, although an important consideration must be made. In the case of fossil fuel co-feeding, the input of fossil carbon must be considered here as a positive term. Furthermore, if there is an input of electricity to the plant, the associated emissions due to the production of the electricity should be included.

[‡] The indirect land-use change happens when agricultural or pasture land previously destined for food, feed and fiber markets is diverted to the production of biofuels, bringing non-agricultural land into production elsewhere to satisfy the non-fuel demand [3].

In the plant (biorefinery), the potential emissions are due to the use of consumables (e.g. catalysts, oil, amines, oxygen) and the import of services (electricity and heat). The incorporation of BECCS to the plant (optional) involves the conditioning (compression) of the CO_2 and therefore the consumption of electricity, which when imported from the grid, gives a net GHG emission. The co-feeding of a fossil fuel (optional) results in an emission of the non-biogenic carbon in the plant, which should be accounted for.

$$e_p = \text{consumables} + \text{import of services (+ CCS) (+ co-feeding)}$$

Table 1. Selected scenarios for the land-use change.

	Reference land use (R)			**Actual land use (A)**		
	w/ bonus[a]	w/o bonus	No change	w/ bonus[a]	w/o bonus	No change
SOC_{ST}	Warm temperate and dry climate with high activity clay soils					
F_{LU}	Cultivated[b]	Cultivated[b]	Managed forest[c]	Managed forest[c]		
F_{MG}	No till	Reduced tillage	All	All		
F_I	Low	Low	All	All		
C_{VEG}	All[d]			Temperate continental forest and mountain systems, Asia and Europe broadleaf ≤20[e]		

[a] This case has a bonus of 29 g CO_2 eq/MJ [2].

[b] *Table 2* of the Commission Decision [3].

[c] *Table 7* of the Commission Decision [3].

[d] *Table 9* of the Commission Decision [3].

[e] *Table 18* of the Commission Decision [3].

2.2. Calculation of E_i

The calculation of E_i requires the allocation of the GWP (global warming potential) of the co-products and services. This allocation is made using the energy content based on the LHV (lower heating value) of each co-product, as the Directive states [2]. However, if electricity and/or heat are added to the list, then there is no explicit indication in the Directive of how to proceed. We propose the allocation of the exported electricity to the grid based on its electric power (MW_e).

The value of e_{td} is provided by the Directive for the equivalent farmed wood for DME synthesis (2 g CO_2/MJ of product) [2]. This value refers to biofuels and therefore the extension of its application to chemicals and electricity is assumed by the authors.

The value of e_u is defined as zero in the Directive [2]. The EU regulation, as well as equivalent regulations, assumes that the emissions of biofuels due to their final use have a neutral impact on GHG emissions. It is assumed that the CO_2 emitted in the combustion of biofuels is equivalent to the CO_2 assimilated by the growth of the biomass used for their production. However, in the combustion of biofuels, as well as in the combustion of petrol gasoline and diesel, there is an important fraction of other gases with GWP like NO_x, CO and VOC. These emissions despite coming from a renewable carbon source should not be neglected, since they have a larger GWP than CO_2. In this study, an approximation of the real value of the GWP of the co-products is given regarding the final use of each co-product.

In the calculation of e_u, the emissions of gases different to CO_2 and with GWP are considered as having a net emission to the atmosphere. These emissions are different in the case of the use of the same fuel as a transportation fuel or as a fuel for heat generation. In the case of chemicals, there is not combustion of the product but a transformation into a different product (or directly used). In this case, the final use of the chemical must be specified along with its GWP. As there is no combustion of the chemical, the carbon content (in g of CO_2 referring to its complete combustion) should be added as a negative contribution in e_u. The average negative contribution producing a chemical also requires the estimation of the emissions of the final disposition of the chemicals (e.g. recycling, landfill). In this study, the emissions due to the final disposition of chemicals (or the final products manufactured using the chemicals, e.g. plastics) are supposed to be a 50% (average) of their equivalent CO_2 content. For electricity, the e_u is assumed zero, since the use of electricity gives no direct emissions.

$e_{u,\ fuels}$ = GHG emissions (except CO_2) of the fuel (g CO_2 eq. / MJ of co-product)
$e_{u,\ chemicals}$ = GHG fossil emissions due to the processing – final disposition (g CO_2 eq. / MJ of co-product)

3. Application to thermochemical biorefineries using DME as a platform chemical

The proposed methodology is applied to the concepts presented in a previous publication [1]. These concepts are different designs of a thermochemical biorefinery using a common feedstock basis of 2140 dry tonnes/day of poplar chips. The co-products were ethanol, DME, methyl acetate and hydrogen, and electricity as service. The cases were named using a combination of letters, which indicates the technology for syngas conditioning (SR: steam reformer, ATR: autothermal reformer, TR: tar reformer), and a number for the chemical route (hydrocarbonylation or carbonylation of DME) and different configurations (changes in the mix of products). In all cases, the selected technology for gasification was an indirectly-heated circulating fluidized gasifier (i-CFB) and the sale of excess heat was disregarded. The incorporation of BECSS is considered for the TR concepts, since they already had a unit for the capture of CO_2 in the conditioning of the syngas. These concepts of a thermochemical biorefinery allow the capture of CO_2 at low cost compared to the rest of the concepts, since only the compression of the CO_2 up to 100 bar (for transportation) is required. Further details for the process design of the concepts are given in [1].

3.1. Calculation of E'

The inventory of the concepts is presented in Table 2, where it can be noted that electricity is imported only in two concepts (TR-04 and TR-05).

Table 3 shows the calculation of e_p. All emissions of CO_2 in the plant have no impact on e_p (all carbon feedstock is biogenic) and therefore only the consumables, catalysts and the import of electricity (when applicable) contribute to e_p. In the case of TR-04 and TR-05 concepts, there is also a contribution of BECCS incorporation, since the compression of the CO_2 is carried out importing more electricity. The calculation of E' is shown in Table 4, where three different cases of the direct land-use change are included.

Table 2. Inventory of the concepts of thermochemical biorefinery. [a]

	Input to the plant (MW)			**Products and services (MW)**						**CO_2 available for sequestration (t/h)**
	Biomass	Electricity	Oxygen[b]	Ethanol	Methyl acetate	DME	Hydrogen	Electricity	TOTAL	
SR-01	500	-	-	192	-	-	-	23	215	-
SR-02	500	-	-	192	-	17	-	2	211	-
SR-03	500	-	-	-	54	118	-	24	196	-
ATR-01	500	-	2	189	-	-	-	7	196	-
ATR-02	500	-	2	187	-	5	-	8	200	-
ATR-03	500	-	2	-	54	133	-	9	196	-
TR-01	500	-	-	157	-	-	-	61	218	23.4
TR-02	500	-	-	157	-	-	77	18	252	23.4
TR-03	500	-	-	111	-	32	-	32	175	23.4
TR-04	500	11	-	111	-	32	77	-	220	23.4
TR-05	500	1	-	-	51	118	77	-	246	23.4
TR-06	500	-	-	-	51	117	-	42	210	23.4

[a] The consumption of electricity for the conditioning of the CO_2 (BECCS) is not included.

[b] The power requirements for air separation are taken from [5]: 160 kWh/t of oxygen. The consumption of oxygen in the ATR concepts is of 12.15 t/h of oxygen.

Table 3. Calculation of e_p.

$g\ CO_2$ eq./MJ	Import of electricity[a]	Oil scrubbing[b]	Catalysts and chemicals[c]	Oxygen for ATR[a]	Incorporation of BECCS[d]	$\mathbf{e_p}$
SR-01	-	1.2	0.4	-	-	1.7
SR-02	-	1.3	0.5	-	-	1.7
SR-03	-	1.3	0.4	-	-	1.7
ATR-01	-	1.4	0.5	1.4	-	3.2
ATR-02	-	1.3	0.5	1.4	-	3.2
ATR-03	-	1.3	0.5	1.4	-	3.1
TR-01	-	-	0.5	-	-	0.5
TR-02	-	-	0.4	-	-	0.4
TR-03	-	-	0.5	-	-	0.5
TR-04	6.9	-	0.4	-	1.6	9.0
TR-05	0.6	-	0.4	-	1.4	2.4
TR-06	-	-	0.4	-	-	0.4

[a] The import of electricity from the grid has a CO_2 emission of 0.5 t/MWh (a typical CO_2 emission per electric MW in Europe).

[b] The oil scrubbing (not applicable for TR concepts) is assumed to use biodiesel with an emission factor of 41 g CO_2 eq/MJ [2].

[c] It includes the catalyst for the syngas cleaning, conditioning and synthesis, and the chemicals for the capture of CO_2 in the TR concepts.

[d] The consumption of electricity (conditioning of CO_2) is translated into a net CO_2 emission as in [a]. The extra consumption is removed from the electricity production (reducing the total production in MJ), except for concepts TR-04 and TR-05 where it can only be imported from the grid.

Table 4. Calculation of E'.

$g\ CO_2$ eq./MJ	e_{ec}	e_l [a]			e_p	e_{ccs}	**E'**		
		w/ bonus	w/o bonus	No change			**w/ bonus**	**w/o bonus**	**No change**
SR-01	5	-43.1	-17.3	0	1.7	-	-36.5	-10.7	6.7
SR-02	5	-43.6	-17.9	0	1.7	-	-36.9	-11.2	6.7
SR-03	5	-43.7	-18.1	0	1.7	-	-37.1	-11.4	6.7
ATR-01	5	-44.7	-19.2	0	3.2	-	-36.5	-11.0	8.2
ATR-02	5	-44.4	-18.8	0	3.2	-	-36.2	-10.7	8.2
ATR-03	5	-43.9	-18.3	0	3.1	-	-35.8	-10.2	8.1
TR-01	5	-42.8	-16.9	0	0.5	31.5	-68.8	-42.9	-26.0
TR-02	5	-41.3	-15.0	0	0.4	27.0	-62.9	-36.7	-21.6
TR-03	5	-46.3	-21.2	0	0.5	39.7	-80.6	-55.5	-34.2
TR-04	5	-43.1	-17.3	0	9.0	29.5	-58.6	-32.8	-15.5
TR-05	5	-41.2	-14.9	0	2.4	26.4	-60.2	-33.9	-19.0
TR-06	5	-42.8	-16.9	0	0.4	32.7	-70.1	-44.2	-27.3

[a] The cases of direct land-use change are explained in the methodology (section 2).

3.2. Calculation of E_m, E_i and savings

For the calculation of E_m, E_i and savings only the case of no direct land-use change is selected, which is the worst scenario.

Table 5 shows the emission factors for each co-product regarding their final use and associated emissions. Besides, information on the emissions corresponding to coal combustion are provided for the assessment of the coal co-feeding within the concepts[§]. Regarding the mix of products, methyl acetate can merely be used as chemical. For the rest, the potential uses are: for ethanol as a transportation fuel (substitute of gasoline) and as a chemical (e.g. production of ethylene or butanol); for DME as a transportation fuel (substitute of diesel), as a fuel for heat production (substitute for LPG) and as a chemical (e.g. substitute of naphtha for olefin production); and for hydrogen as a fuel for electricity generation and a chemical. For the calculation of the emission of each co-product and electricity, it is necessary to allocate the common emissions (E'). Table 6 shows the allocated emission up to the biorefinery (E_i), as well as the individual savings regarding the final use (the values are given per MJ of co-product or electricity).

Table 7 presents the values of E_m (GHG emissions, cradle to grave) and E (GHG emissions, cradle to gate, since the final use of the bio-products is disregarded). Moreover, the average saving and the extra saving (g CO_2 per MJ of total products and services) are shown for the three different scenarios of final use of the mix of products: maximum production of transportation fuels, maximum production of other fuels (heat and electricity) and maximum production of chemicals. The saving of GHG emissions for each concept is larger than that required in the European regulation for biofuels (transportation fuels and fuels for heat and electricity production) for 2018 (see Figure 1). It is even higher in the case of considering chemicals forced to fulfill the same requirement as fuels.

The translation of the extra savings into an economic benefit has two alternatives without compromising the sustainability of the biorefinery: the sale of CO_2 credits and the co-feeding of coal. Table 8 shows the results for both alternatives, which correspond to the extra-avoided emissions (t/h of CO_2) and to the amount of feedstock that can be substituted by coal (MW of coal).

[§] The co-feeding of coal in the gasifier requires further discussion and it is outside the scope of this study. Nonetheless, the amount of fossil fuels that can be used in the biorefinery, regardless of the fuel and how it is processed, can be calculated using the proposed methodology.

Table 5. Emission factors and emissions in the use of products for the assessment of GHG savings.

g CO_2 eq/MJ	E_{Fi}				e_u (fuel)	e_u (chemical)	
	Transportation fuel [2]	Heat generation [2]	Electricity generation [2]	Chemical	Use as fuel [a]	Processing	Complete combustion
Ethanol	83.8	-	-	25.4 [6]	17.7	7.7 [7]	70.1
DME	83.8	77.0	-	73.3	18.9	7.7[b]	68.3
Methyl acetate	-	-	-	25.4[b]	-	7.7[b]	90.3
Hydrogen	91.0	-	91.0	91.0[c]	0	0	0
Electricity [d]	-	-	91.0	-	-	-	-
Coal	-	-	-	-	-	-	100.5[e]

[a] These values are calculated using references [8, 9] for the emissions of GHG different to CO_2.

[b] It is assumed the same value than ethanol.

[c] It is assumed the same value as for electricity generation.

[d] The emission factor for electricity is the same as the factor for the production of electricity using fossil fuels.

[e] Medium value for a coal with 68.5% (w.) of C and a heating value of 25 MJ/kg dry.

Table 6. Allocated emissions (E_i) and savings for each concept of thermochemical biorefinery.

	Ethanol				**DME**						**Methyl acetate**		**Hydrogen**		**Electricity**		**Directive 2009/28/EC**	
g CO_2 eq./MJ	Fuel (transportation)		Chemical		Fuel (transportation)		Fuel (heat)		Chemical		Chemical		Fuel (electricity)		-		-	
of i	E_i	Saving	E_i	Saving	E_i	Saving	E_i	Saving	E_i	Saving	E_i	Saving	E_i	Saving	E_i	Saving	E	Saving[a]
SR-01	25.5	70%	-19.9	178%	-	-	-	-	-	-	-	-	-	-	2.8	97%	8.7	90%
SR-02	25.8	69%	-19.7	177%	21.5	74%	21.5	72%	-23.9	133%	-	-	-	-	2.1	98%	8.7	90%
SR-03	-	-	-	-	25.2	70%	25.2	67%	-20.2	128%	-34.1	234%	-	-	3.0	97%	8.7	88%
ATR-01	27.6	67%	-17.9	170%	-	-	-	-	-	-	-	-	-	-	2.4	97%	10.2	88%
ATR-02	27.3	67%	-18.2	171%	21.1	75%	21.1	73%	-24.3	133%	-	-	-	-	2.4	97%	10.2	88%
ATR-03	-	-	-	-	26.9	68%	26.9	65%	-18.5	125%	-33.8	233%	-	-	2.4	97%	10.1	86%
TR-01	1.9	98%	-43.6	272%	-	-	-	-	-	-	-	-	-	-	-6.2	107%	-22.8	126%
TR-02	6.3	92%	-39.1	254%	-	-	-	-	-	-	-	-	-4.5	105%	0.2	100%	-18.7	122%
TR-03	-1.3	102%	-46.8	284%	14.7	82%	14.7	81%	-30.7	142%	-	-	-	-	-5.0	105%	-30.2	135%
TR-04	11.9	86%	-33.6	232%	18.6	78%	18.6	76%	-26.8	137%	-	-	-3.4	104%	-	-	-16.3	119%
TR-05	-	-	-	-	11.1	87%	11.1	86%	-34.3	147%	-38.5	252%	-4.1	105%	-	-	-17.2	122%
TR-06	-	-	-	-	4.9	94%	4.9	94%	-40.5	155%	-40.4	259%	-	-	-4.4	105%	-23.9	132%

Table 7. GHG emissions (E_m and E) and extra saving for each concept of thermochemical biorefinery.

g CO_2 eq./MJ	**Max. production of transportation fuels**			**Max. production of other fuels**			**Max. production of chemicals**			**Directive 2009/28/EC**		
	E_m	Medium saving (%)	Extra saving	E_m	Medium saving (%)	Extra saving	E_m	Medium saving (%)	Extra saving	E	Medium saving (%)	Extra saving
SR-01	24.2	73%	26.7	24.2	73%	26.7	-15.6	168%	35.8	8.7	90%	42.2
SR-02	26.4	70%	23.9	26.4	70%	23.6	-18.6	173%	36.7	8.7	90%	41.6
SR-03	3.6	145%	40.0	3.6	143%	37.3	-16.2	145%	55.8	8.7	88%	34.9
ATR-01	27.2	68%	23.3	27.2	68%	23.3	-16.3	167%	33.3	10.2	88%	40.2
ATR-02	27.1	69%	23.3	27.1	69%	23.2	-16.3	167%	34.1	10.2	88%	40.3
ATR-03	6.6	142%	36.6	6.6	140%	33.6	-17.2	146%	55.8	10.1	86%	33.0
TR-01	-11.9	101%	63.5	-11.9	101%	63.5	-43.1	220%	70.7	-24.0	128%	75.7
TR-02	-8.7	97%	60.6	-8.7	97%	60.6	-36.8	197%	67.1	-19.6	123%	71.5
TR-03	-17.9	99%	69.1	-17.9	99%	68.3	-54.1	222%	82.6	-32.2	138%	83.4
TR-04	-1.8	91%	53.5	-1.8	91%	52.9	-31.5	174%	64.6	-13.5	116%	65.3
TR-05	-13.2	119%	59.3	-13.2	118%	57.2	-36.7	150%	79.5	-17.0	122%	63.1
TR-06	-21.0	126%	66.0	-21.0	126%	63.6	-47.6	162%	88.8	-25.3	134%	70.3

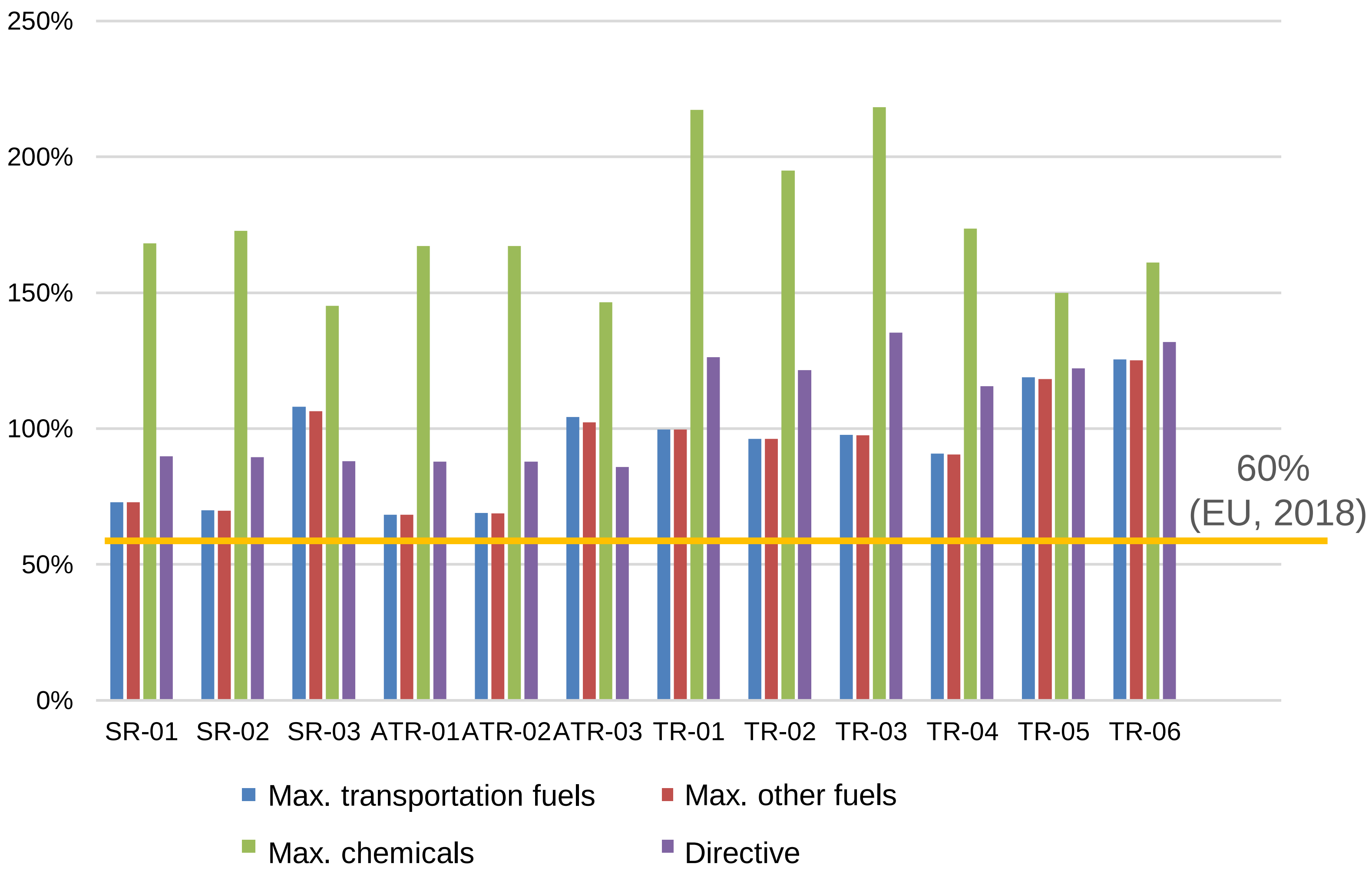

Figure 1. Average saving of each concept considering the final use of co-products (transportation fuels, other fuels and chemicals) or not (Directive).

Table 8. Extra-avoided emissions and co-feeding of coal.

	Extra-avoided emissions (t CO_2 eq./h)				**Co-feeding (MW of coal)**			
	Max. production of transportation fuels	Max. production of other fuels	Max. production of chemicals	Directive 2009/28/EC	Max. production of transportation fuels	Max. production of other fuels	Max. production of chemicals	Directive 2009/28/EC
SR-01	20.63	20.63	27.71	32.63	51	51	66	76
SR-02	18.20	17.94	27.88	31.59	46	45	67	74
SR-03	28.21	26.35	39.35	24.64	67	64	89	60
ATR-01	16.42	16.42	23.48	28.38	42	42	57	68
ATR-02	16.80	16.72	24.55	29.01	42	42	60	69
ATR-03	25.80	23.68	39.34	23.30	62	58	89	57
TR-01	47.16	47.16	52.49	56.19	103	103	112	119
TR-02	52.42	52.42	58.01	61.89	112	112	121	127
TR-03	40.61	40.18	48.56	49.02	92	91	106	107
TR-04	42.39	41.91	51.20	51.72	95	94	110	111
TR-05	52.50	50.63	70.44	55.87	112	109	140	118
TR-06	47.12	45.41	63.43	50.17	103	100	130	109

4. Impact on the profitability of the concepts

In the assessment of the impact, only the scenario of the Directive (i.e. the final use of the co-products is disregarded) is analyzed. The results of the sustainability assessment show that there is either potential for an enhancement of the revenue (sale of extra-avoided emissions) or a reduction of the operating cost (co-feeding of coal). For instance, the profitability of the concepts should be updated in order to consider these alternatives.

The calculation of the IRR (internal rate of return) has been updated from the previous publication [1], where further details of the methodology (for the calculation of investment and operating cost) can be found. Table 9 shows a summary of the most important parameters. The exchange rate $/€ is assumed to be 1.35. Only for the TR concepts, which incorporate BECCS, is there a slight modification of the investment and operating cost. Table 10 presents the updated investment and operating costs along with the resulting total costs of sequestration of CO_2 for each concept.

Table 9. Economic assumptions for discounted cash flow analysis.

Parameter	Value
Debt/Equity	0/100%
Plant life	20 years
Depreciation (linear)	10 years
Salvage value	0 M USD
Construction period	1 year
Income tax	30%
Working capital	1-month operating costs
Land	6% TIC

Working capital and cost of land are recovered at the end of plant life.

Table 10. Modification of the economic results of BECCS incorporation to the TR concepts (from [1]).

	Increment of capital investment (M$)	Increment of operating cost (M$/year)[a]	Reduction of revenue (M$/year)[b]	Total cost of CO_2 sequestration (€/t)[c]
TR-01	6.0	-	1.1	21.9
TR-02	6.0	-	1.1	21.7
TR-03	6.0	-	1.1	21.9
TR-04	6.0	1.1	-	22.1
TR-05	6.0	1.1	-	24.4
TR-06	6.0	-	1.1	24.4

[a] The import of electricity is assumed to have a cost of 5c$/kWh (same for export).

[b] The export of electricity is reduced by the compression of the CO_2 for sequestration. The sale of extra-avoided emissions (with a positive effect on the revenue) is excluded in order to show the impact of BECCS incorporation to the plant.

[c] It includes the cost of CO_2 compression within the plant, the cost of transportation and the cost of sequestration. The transport and sequestration of the CO_2 have a cost of 4 and 14 €/t respectively [10].

4.1. Extra-avoided emissions (increment in revenue)

The sale of the extra-avoided emissions results in an increment in the IRR (via revenue) for each concept. Figure 2 shows the sensibility of the IRR for the price of the CO_2 credits in the emission trading.

The sale of the extra-avoided emissions does not require an increment in the investment or operating cost of the plant, except for the TR concepts where a fraction of the extra-avoided emissions corresponds to sequestrated CO_2 (negative emissions). Therefore, for all concepts except the TR's, there is not a minimum price for the CO_2 credit. The plant would benefit regardless of the price of the credit. In the TR concepts, the minimum sale price for the CO_2 is about 5.5 €/t, which is that required in order to get the same IRR as in the base case without BECCS incorporation [1]. This price is much lower than the operating cost of sequestration (Table 10) and lower than the cost of transportation and sequestration of CO_2 (see Figure 2).

4.2. Co-feeding of coal[**]

The co-feeding of coal results in a slight increment (from 1 to 2 points) of the IRR (via reduction of operating costs) for each concept. The impact of the co-feeding of coal depends on the price of coal, which contrary to the price of the CO_2 credit, could be assumed to be constant. Therefore, the substitution of biomass (3.3 $/GJ) with coal has a limited impact (the co-feeding represents from 12 to 26% of the total feedstock), which is shown in Table 11. The resulting increment of the IRR is equivalent to the sale of extra-avoided emissions with a CO_2 credit price of about 20 €/t. Hence, in the case of lower prices of the credit, the co-feeding of coal would generate the greatest profitability.

Table 11. IRR for the co-feeding of coal.

Concept	Base case [1]	Co-feeding of coal
SR-01	10.44%	11.68%
SR-02	12.06%	13.25%
SR-03	23.34%	24.03%
ATR-01	9.17%	10.52%
ATR-02	9.85%	11.19%
ATR-03	28.74%	29.51%
TR-01	5.41%	6.95%
TR-02	7.59%	9.34%
TR-03	1.38%	3.02%
TR-04	4.57%	6.21%
TR-05	23.90%	24.79%
TR-06	20.28%	21.05%

[**] In the assessment of the co-feeding of coal, it has been assumed that there is not a change of equipment, i.e. the gasifier does not change, and that the H2/CO ratio of the syngas is the same. Of course, this is only a rough estimation that should be further investigated.

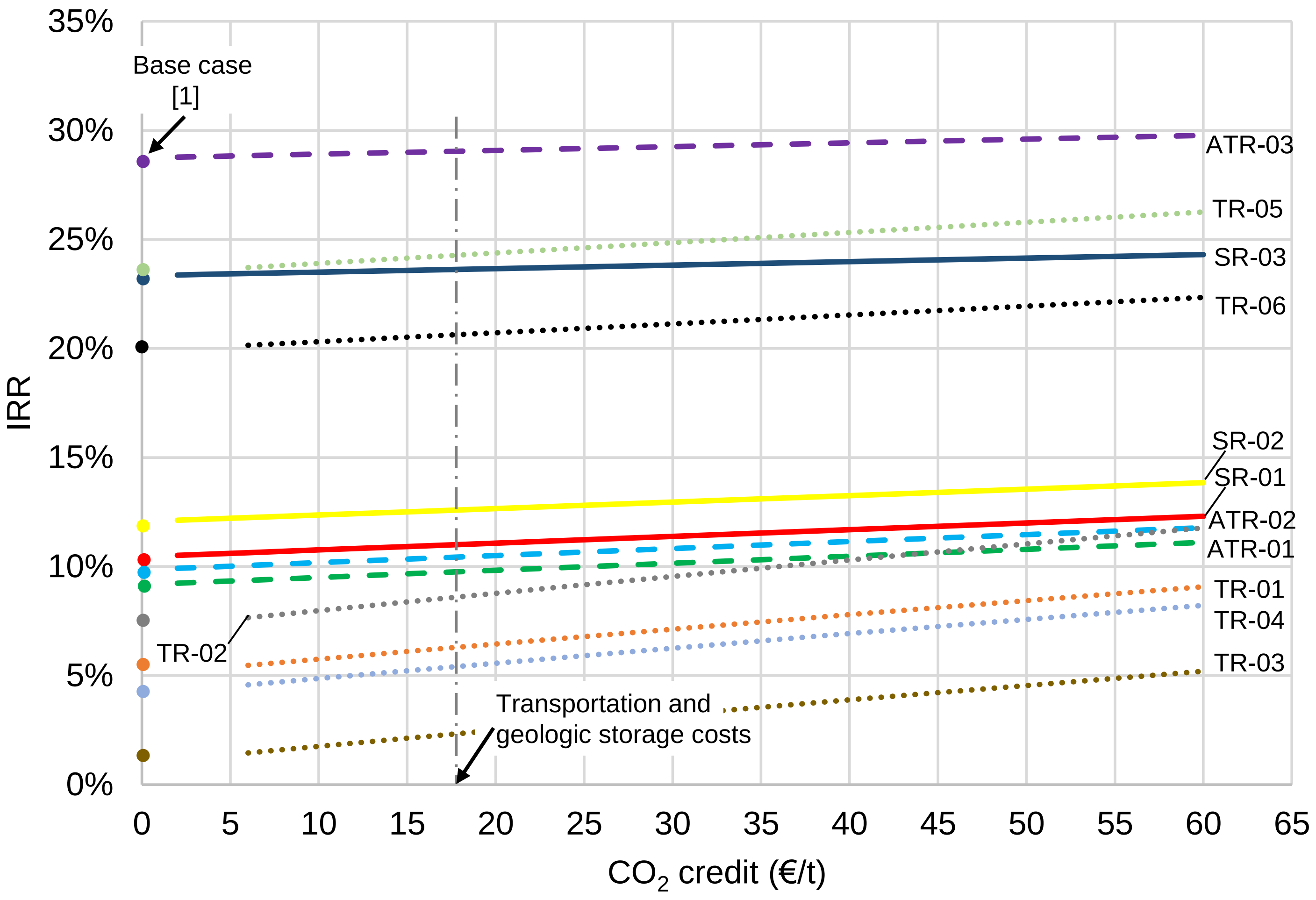

Figure 2. Sensibility of the profitability of the plant for the price of CO_2 credits.

5. Discussion

The European Environment Agency (EEA) has stated that the release of the carbon content (in the form of CO_2) from biomass used for energy proposes could result in a carbon accumulation in the atmosphere [11]. Such accumulation would be due to indirect land-use change, which has not yet been regulated by the EU [12]. This study has not included indirect land-use change. However, when the EU states a methodology for the calculation of indirect land-use change, it can be incorporated including a new term in our methodology.

In our proposed methodology, the inclusion of chemicals implies that the calculation of the emissions in the final use of the bio-products cannot be assumed zero, as the European Directive states [2]. Indeed, the benefit of chemical co-production relies on the negative value of the emissions in their final use. As chemicals are not combusted, their carbon content is at least partially storage. Further research on the final disposition for each chemical could determine the individual value for each final use. In this study, however, a conservative average factor for their final disposition (50%) has been used instead of an individual factor for each chemical. In the case of biofuels, the emissions in their final use must not be disregarded either. This study shows that if the final use of biofuels were not taken into account, there would be an overestimation of the potential saving of a thermochemical biorefinery, since the use of biofuels involves greater GHG emissions than the equivalent CO_2 of the complete combustion.

For the incorporation of BECCS, there is a benefit with respect to the capture in conventional power plants which have greater sequestration costs (about 100 \$/t of CO_2) [10]. The resulting operating costs for the sequestration of CO_2 are highly competitive (20-30 €/t) although still not commercial. The CO_2 sequestrated via BECCS are negative emissions, since they constitute a net outlet of CO_2 from the atmosphere. The negative emissions can be sold as extra revenue in emission trading. However, in the assessed concepts, the net emissions are lower than required in order to achieve sustainability. In this study, the whole extra-avoided emissions have been considered for the calculation of the impact on the economy.

If the extra-avoided emissions are considered, the sale of CO_2 credits is favorable and not constrained to the cases with BECCS, but for all concepts (without modification of the process). However, this possibility depends on future regulation. Another alternative is the co-feeding of coal, which can be afforded under current regulations and does not depend on future regulation of the CO_2 market. However, there are important considerations regarding the technical viability of the co-feeding. The biomass/coal ratio is low and these are not the common values for co-feeding in gasifiers. In the co-feeding of coal, it has been implicitly assumed that the carbon content of the coal is completely emitted to the atmosphere as CO_2. For instance, it is assumed that there is no carbon from the coal in those products that are not combusted in their final use, i.e. chemicals. Hence, in the case of chemicals as co-products the co-feeding of coal could be larger than the figure calculated.

6. Conclusions

This study proposes a methodology for the assessment of sustainability in thermochemical biorefineries with multiproduction, which aims to overcome the lack of current European regulation. The proposed methodology is validated by the assessment of a set of different concepts of a thermochemical biorefinery with multiproduction, which were previously published. All concepts of a thermochemical biorefinery achieve profitability using the methodology of European regulation and the methodology proposed in this study.

The co-production of chemicals results in a great benefit for both the fulfillment of sustainability and the enhancement of profitability. Chemicals are able to achieve the saving in GHG emissions fixed by the EU and even savings of over 200%, since they are not combusted in their final use. Therefore, chemicals represent a storage of carbon, which has not been previously assessed. The economic valorization of this storage, along with the incorporation of carbon capture and sequestration in the plant (BECCS), could be carried out via the sale of CO_2 credits or co-feeding of fossil fuels.

Acknowledgments

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Annex A

Supplementary Information of Paper 5*

Summary

1. Detailed configuration for each polygeneration concept
2. Modeling of the main equipment (Aspen Plus)
3. Material and energy balances
4. Calculation of fixed capital cost and operating costs

References

A.1. Detailed configuration for each polygeneration concept

The process flow diagram of the 12 assessed concepts is presented below. The process flow diagrams show the specific plant process configuration for each concept.

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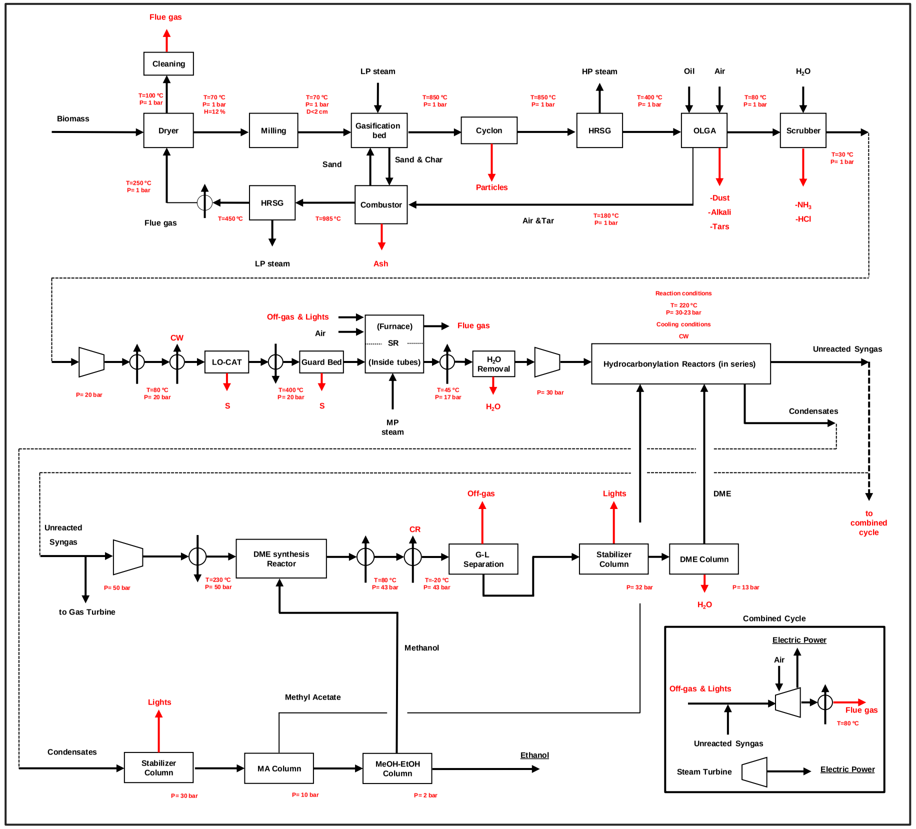

Figure A.1. Process flow diagram for SR-01.

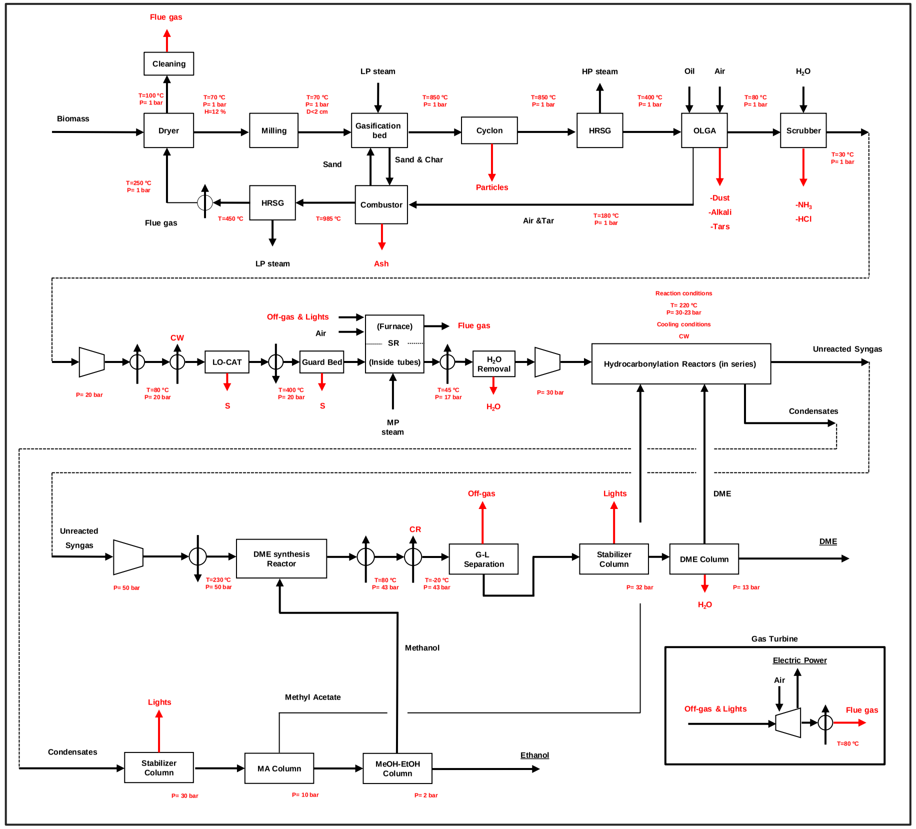

Figure A.2. Process flow diagram for SR-02.

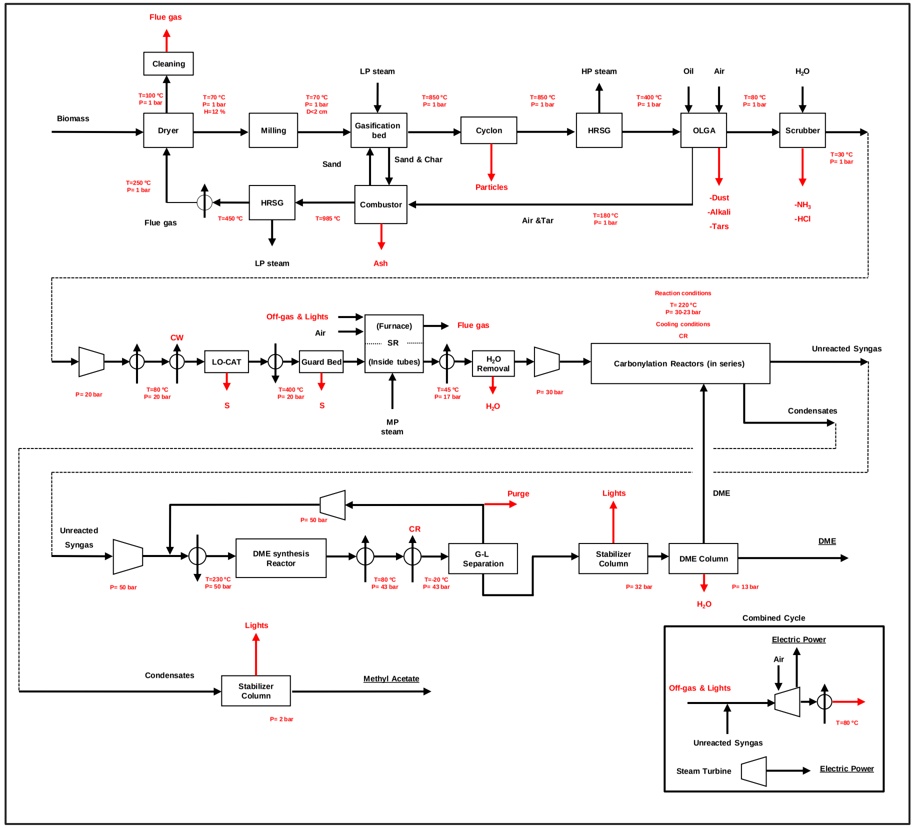

Figure A.3. Process flow diagram for SR-03.

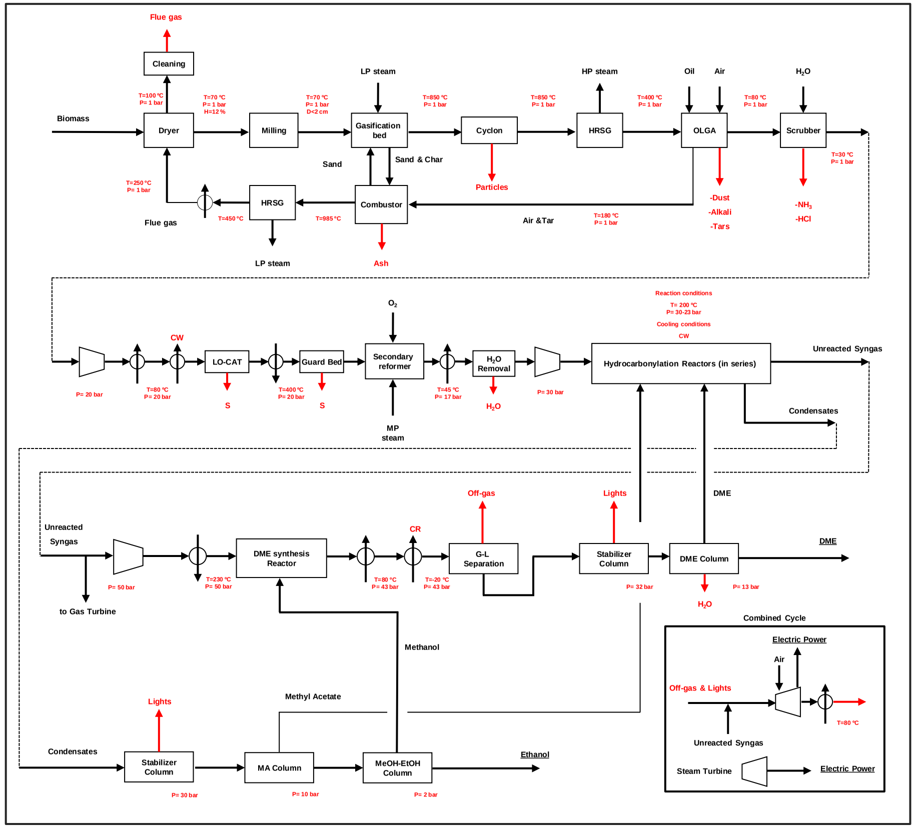

Figure A.4. Process flow diagram for ATR-01.

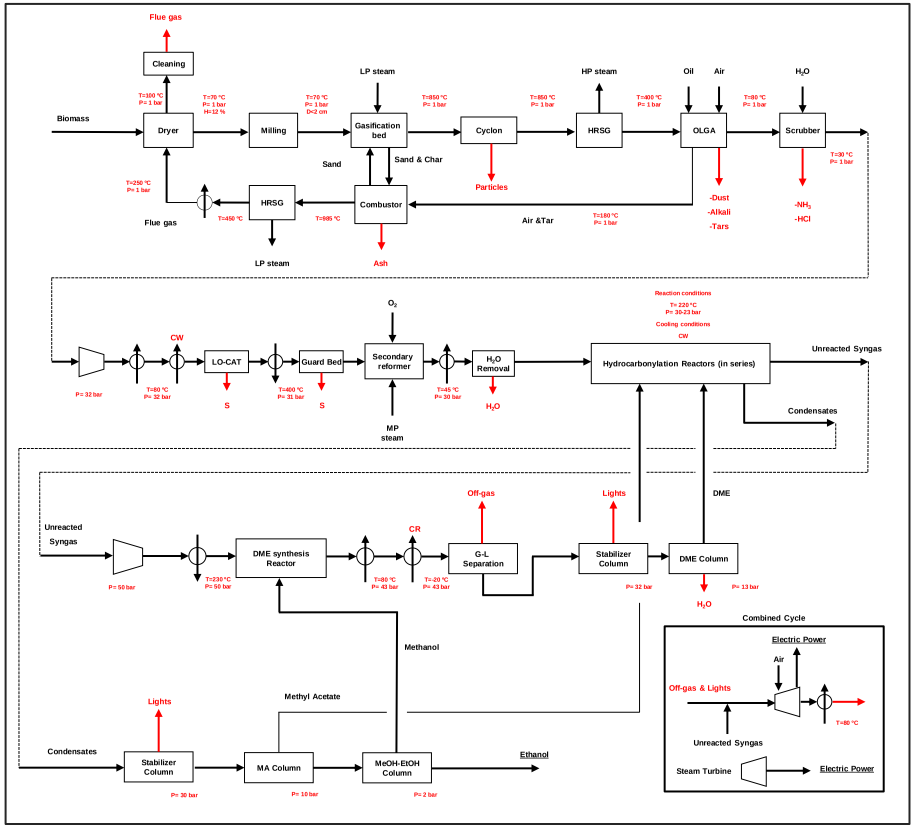

Figure A.5. Process flow diagram for ATR-02.

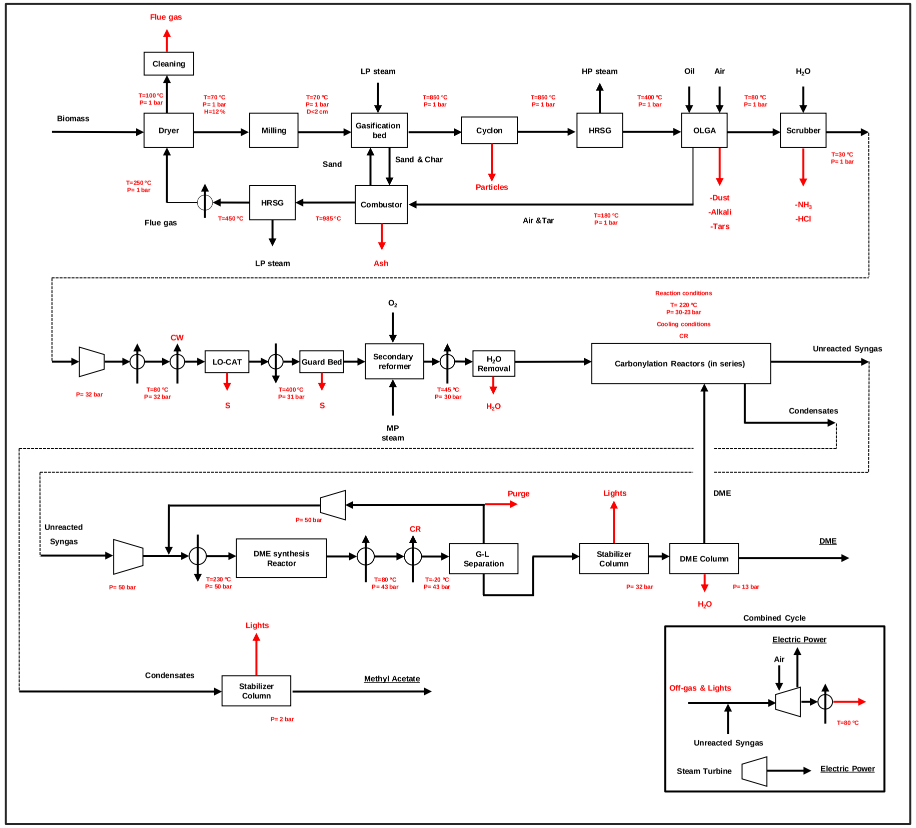

Figure A.6. Process flow diagram for ATR-03.

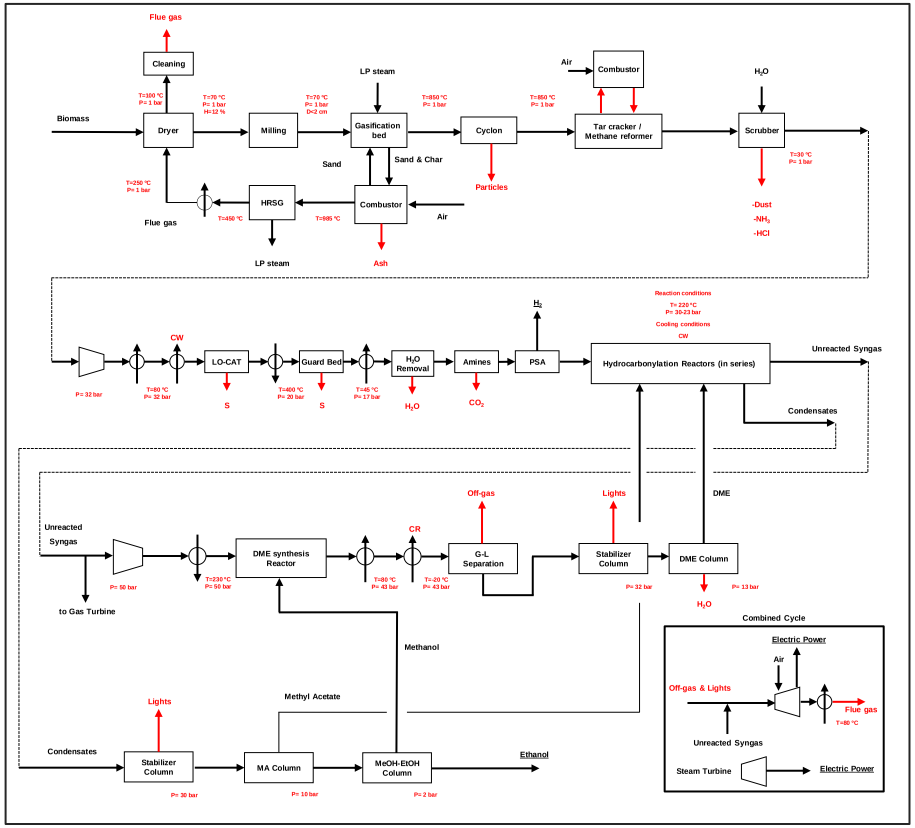

Figure A.7. Process flow diagram for TR-01.

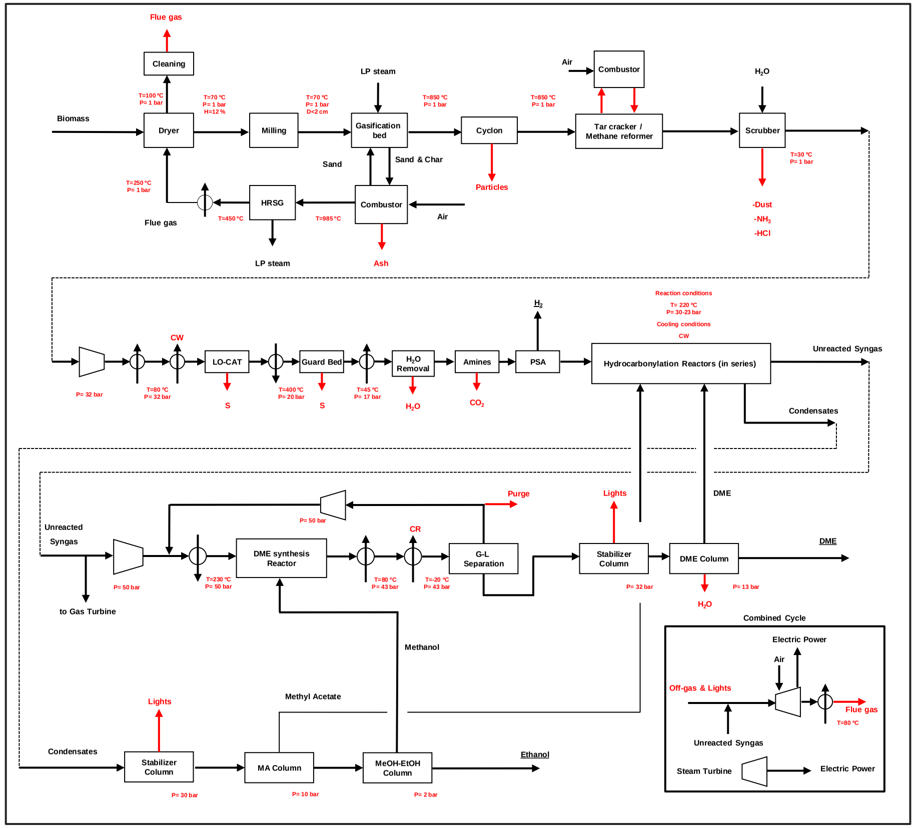

Figure A.8. Process flow diagram for TR-02.

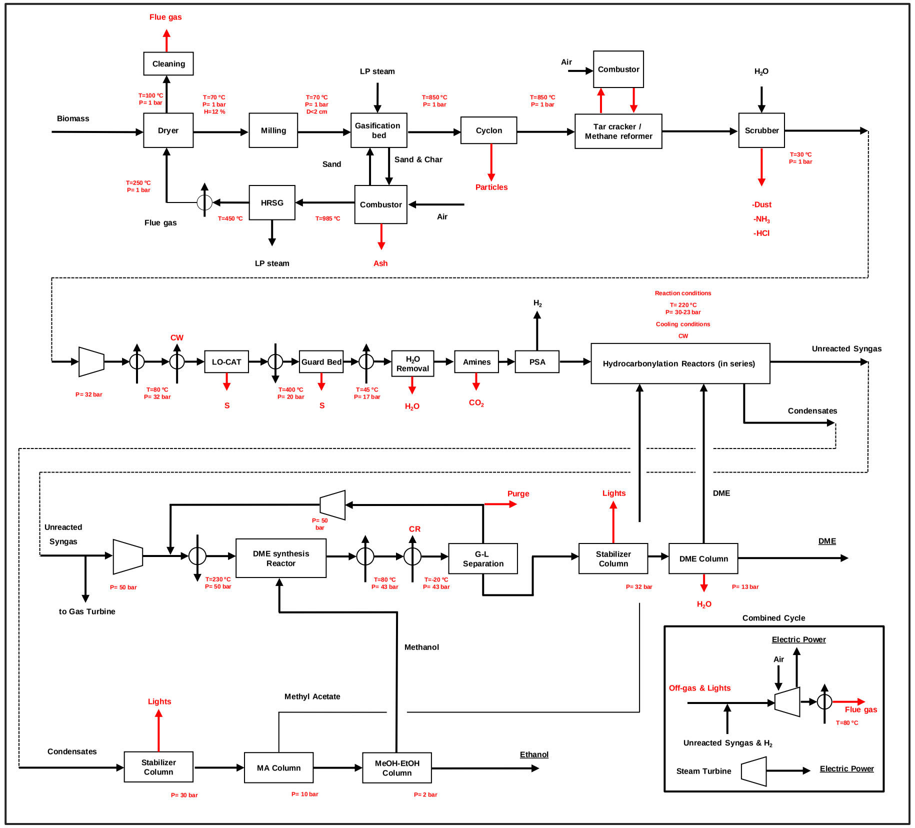

Figure A.9. Process flow diagram for TR-03.

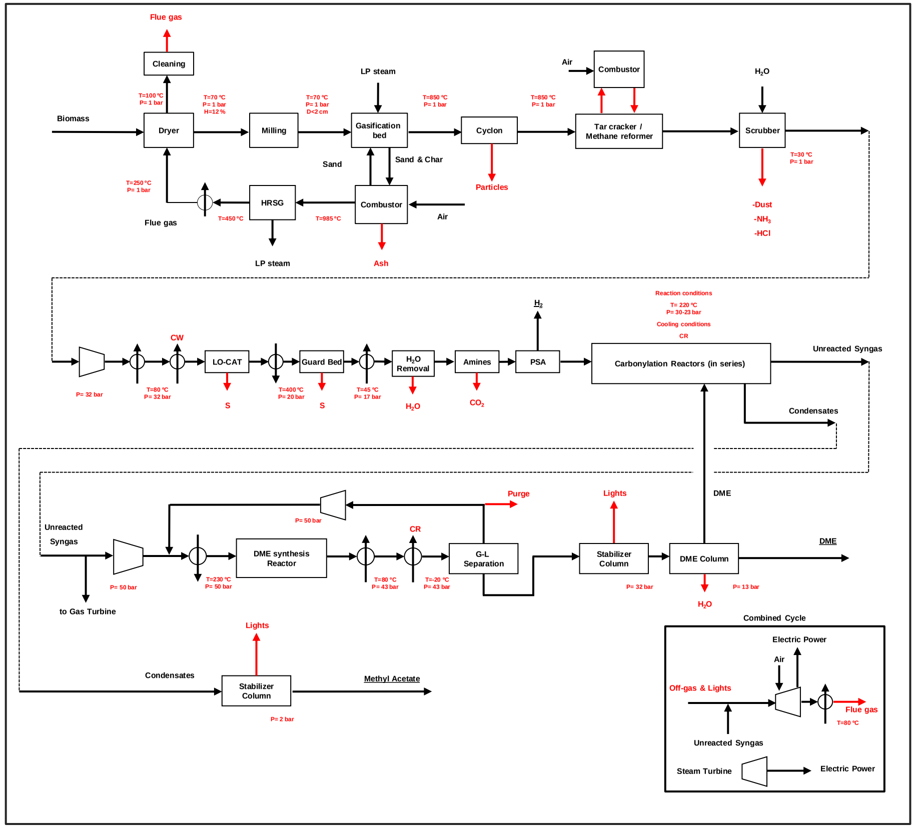

Figure A.10. Process flow diagram for TR-04.

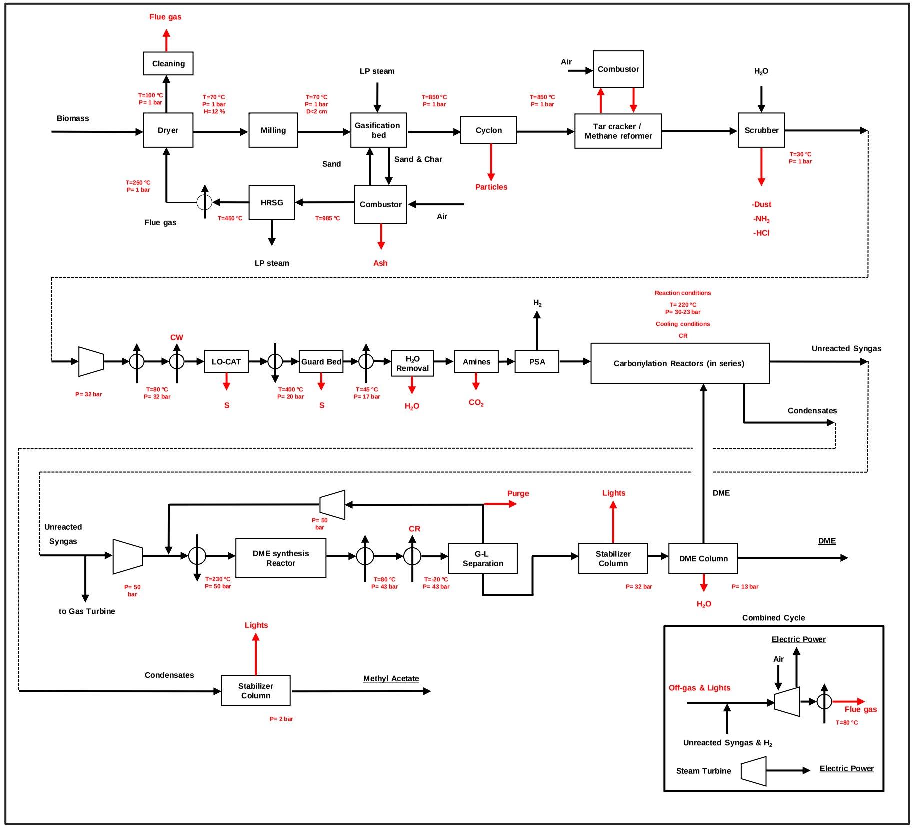

Figure A.11. Process flow diagram for TR-05.

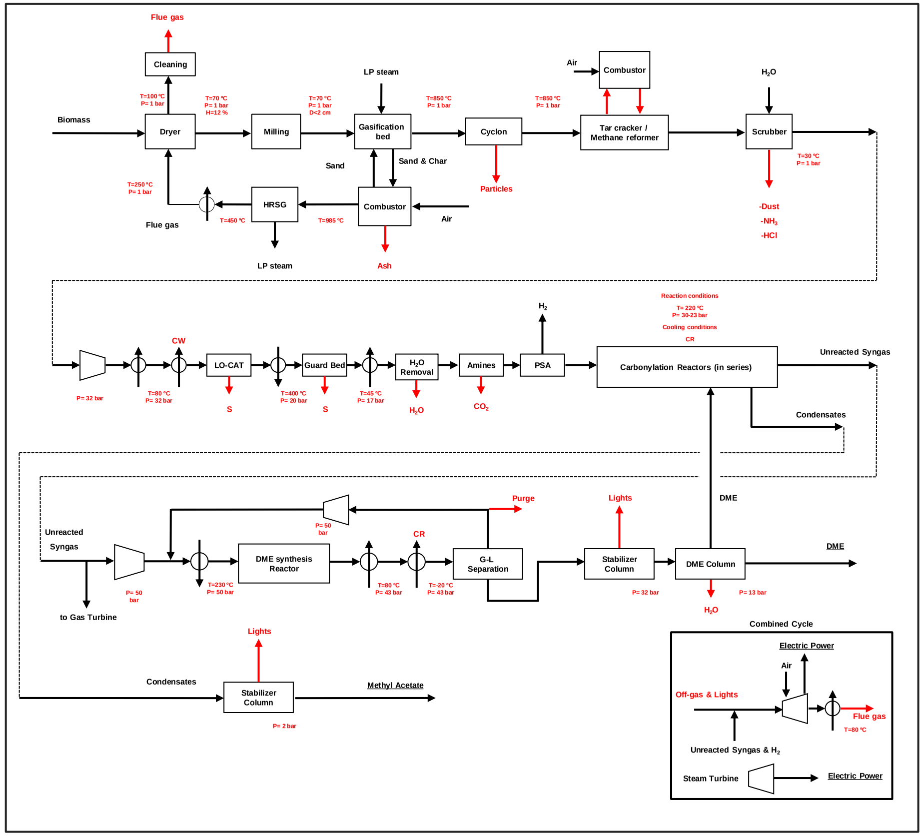

Figure A.12. Process flow diagram for TR-06.

A.2. Modeling of the main equipment (Aspen Plus)

The modeling of the main equipment is presented below. All simulations were carried out using Aspen Plus software (AspenTech), version 2006.5. Non reference data for simulated equipment was supposed regarding to the *state of the art*.

Table 2.1. Modeling of main process units.

Equipment	Parameter	Value
Heat Exchangers	Pressure drop	3 psi
Pumps	Mechanical Efficiency	0.90
Compressors	Isentropic efficiency	0.78
	Max. pressure ratio	3.5
Process Turbines	Isentropic efficiency	0.72
Gas Turbine	Isentropic efficiency	0.90
Steam Turbine	Isentropic efficiency	0.72
SR (steam reformer) (Modeled as a RGibbs)	Pressure	17 bar
	Temperature	900 ºC
	Reactions	Chemical equilibrium (ΔT = 20 ºF)
	molar H_2O/C	1.22
ATR (secondary reformer) (Modeled as a RGibbs)	Pressure	32 bar
	Temperature	995 ºC
	Reactions	Chemical equilibrium (ΔT = 20 ºF)
	molar H_2O/C	1.40
	molar O_2/C	0.46
Tar cracker / methane reformer [1] (Modeled as a RStoic and a REquil)	Pressure	1.4 bar
	Temperature	930 ºC
	Reactions	1) $CH4 + H_2O \rightarrow CO + 3H_2$ 2) $C_2H_2 + 2H_2O \rightarrow 2CO + 3H_2$ 3) $C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$ 4) $C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2$ 5) $TAR + 10H_2O \rightarrow 10CO + 14H_2$ 6) $2NH_3 \rightarrow N_2 + 3H_2$ 7) $CO + H_2O \rightarrow CO_2 + H_2$
	Molar conversions	Reaction 1: 91.4% Reaction 2, 3, 4, 5: 97.2% Reaction 6: 90.0% Reaction 7: equilibrium at 930ºC

DME synthesis reactor [2] (Modeled as a RStoic)	Pressure	50 bar
	Temperature	250 ºC
	Reactions	1) $3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2$ 2) $CO + 2H_2 \rightarrow CH_3OH$ 3) $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ 4) $CH_3COOCH_3 + 2H_2 \rightarrow CH_3OH + C_2H_5OH$
	CO per-pass conversion	52.25% (reaction 1) 2.75% (reaction 2)
	MeOH per-pass conversion	100% (reaction 3)
	MA per-pass conversion	100% (reaction 4)
	H_2/CO molar ratio	variable (0.5-1.5)
	Pressure drop	3.3 bar
Hydrocarbonylation reactors [3] (5 reactors in series; modeled as a RStoic)	Pressure	30-20 bar
	Temperature	220 ºC
	H_2/CO molar ratio	1
	Reactions	1) $CO + 1.464\ H_2 + 0.4096\ CH_3OCH_3 \rightarrow 0.5422\ CH_3OH + 0.4578\ C_2H_5OH + 0.07831\ CH_3COOCH_3 + 0.1265\ CO_2$ 2) $CH_3COOCH_3 + 2\ H_2 \rightarrow CH_3OH + C_2H_5OH$
	CO per-pass conversion	48.0% (reaction 1)
	MA per-pass conversion	100% (reaction 2)
	Pressure drop	10 psi
Carbonylation reactors [4] (5 reactors in series; modeled as a RStoic)	Pressure	30-20 bar
	Temperature	220 ºC
	H_2/CO molar ratio	1
	Reactions	1) $1.032\ CO + CH_3OCH_3 \rightarrow 0.9366\ CH_3COOCH_3 + 0.04754\ CH_3COOCH_2CH_3 + 0.03169\ CO_2$
	CO per-pass conversion	83.1%
	Pressure drop	10 psi
Cryogenic Refrigeration (CR)	Refrigerant	NH_3
	Number of compressing steps	3
	Temperature of service	-39 ºC

A.3. Material and energy balances

Table 3.1. Amount of products and electricity ready to be sold in each process concept.

	Products (kg/year)				Electricity (kWh/year)
	EtOH	MA	DME	H_2	
SR-01	174,137,360	0	0	0	186,211,272
SR-02	174,297,280	0	15,595,720	0	14,637,608
SR-03	0	74,200,094	107,303,048	0	189,631,026
ATR-01	171,646,800	0	0	0	57,544,067
ATR-02	170,239,280	0	4,781,840	0	60,147,818
ATR-03	0	74,134,079	120,820,375	0	70,233,242
TR-01	142,425,920	0	0	0	488,218,808
TR-02	142,425,920	0	0	15,510,480	141,904,849
TR-03	101,051,280	0	28,807,440	0	252,575,447
TR-04	101,051,280	0	28,807,440	15,510,480	0
TR-05	0	70,485,141	106,946,961	15,510,480	0
TR-06	0	70,486,485	106,654,592	0	333,606,813

A.4. Calculation of fixed capital cost and operating costs

Results from the process simulations were used to estimate capital and operating costs. Purchase costs for equipment (PEC) are taken from published BTL/G studies and vendor quotes (Table 4.1). First, the purchase costs are scaled and the effect of inflation is corrected by using the CEPCI index. Then, the installed equipment cost is calculated by multiplying the purchase cost by an installation factor. If the installation factor is unknown it is assumed 2.47 according to Table 4.1. Thus, the total installed cost (TIC) is calculated by adding up the cost of the individual equipment. The indirect costs are estimated as percentages of TIC as shown in Table 4.2, giving the total plant investment (TPI).

The operating costs are calculated according to Table 4.3. Fixed operating costs are calculated as a percentage of TIC while variable operating costs are calculated based on the cost of the consumables.

Table 4.1. Data for capital cost calculations of the most important equipment.

Unit	**Base purchase cost (MUSD$_{2010}$)**	**Reference year**	**Scale factor (n)**	**Units**	**Base Scale**	**Installation factor**	**Reference**
Grinding	0.13	2003	NA	wet tonne/hour	-	2.47	Supplier
Dryer	0.39	2009	0.70	dry tonne/day	1100	1	Internal
Indirectly-heated CFBG	27.3	2008	0.70	dry tonne/day	550	1	supplier
TR	2.21	2002	0.65	lb/h	75,442	2.47	[5]
TR (regenerator)	2.43	2002	0.65	lb/h	75,442	2.47	[5]
Candle filter	2.70	2008	0.70	-	-	2.47	supplier
OLGA^{TM}	-	2008	-	Nm^3/h	NA	-	supplier [6]
Scrubber	0.165	1995	0.70	m^3/s	NA	1	[7]
Syngas compressor	5.85	2009	0.70	MW_e	5.44	1.32	supplier
LO-CAT^{TM}	1.00	2002	0.65	lb/h	NA	2.47	[8]
Guard bed	0.022	2002	1	Nm^3/s	NA	3	[9]
SR	41.0	2002	0.60	kmol total reformed/hour	1277	1	[10]
ATR	31.02	2009	0.67	Nm^3/h	144	1	[11]
PSA	5.46	2003	0.74	kmol of purge/s	0.29	1.2	[12]
PSA (purge compressor)	4.83	2003	0.67	MW_e	10	1.2	[12]
Amine CO_2 capture system	15.4	2001	0.65	lb CO_2/hour	100,203	2.47	[13]
DME synthesis section[†]	36.79	2009	0.65	mol of feed gas/s	2910	2.10	[14]
DME hydrocarbonylation reactor[‡]							
DME carbonylation reactor[§]							
Gas-liquid separator	0.097	2008	-	MW_{th}	1.81	-	supplier
Stabilizer column[**]							

[†] Includes DME synthesis reactor, gas-liquid separator, stabilizer column, DME purification and cryogenic refrigeration.

[‡] The DME hydrocarbonylation reactor is considered a pressurized vessel for cost estimation purposes and it is size by the GSHV of the catalyst in a similar as [15].

[§] The DME carbonylation reactor is cost-estimated analogously as the DME hydrocarbonylation reactor.

[**] The purchase cost of the stabilizer and distillation columns is estimated as described in [16].

Distillation column[††]							
Expansion turbine	4.71	2002	0.70	MW$_e$	10.30	2	[9]
Air compressor	5.85	2009	0.70	MW$_e$	5.44	1.32	supplier
Gas turbine, combustor and HRSG	19.09	2003	0.70	MW$_e$	26.3	1	[9]
Steam turbine	23.25	2007	0.70	MW$_e$	50	1	supplier
Heat Exchangers[‡‡]							

Scaling equation: Cost/Cost$_{base}$=(Scale/Scale$_{base}$)^n.

The installation factor is 1 if the base cost already includes the indirect costs.

NA: not applicable.

Table 4.2. Cost factors for estimating the TPI from the purchase cost equipment (PEC) and the total installed cost (TIC).

Direct Cost	**% PEC**
Purchase equipment installation	39
Instrumentation and control	26
Piping	31
Electrical systems	10
Building (including services)	29
Yard improvements	12
Total direct costs	147
Indirect Costs	**% TIC**
Engineering design and procurement	7.9
Contractor Management and control	2.2
Capital spares and other costs	2.0
Operator training	1.0
Start up assistance	1.0
EPC constructor contingency	15.0
Total indirect costs	29.1

[††] See above.

[‡‡] The purchase cost of the heat exchanger is calculated as described in [15].

Table 4.3. Data for the estimation of the TOC.

Fixed operating costs	**% TIC**
Labor	1.56
Maintenance	1.50
General expenses	3.07
Management and operation services	0.44
Cost of Goods Sold- Marketing, Logistics and others	1.32
Insurance	0.50
Total	8.39
Variable operating costs	
Biomass (USD_{2010}/tonne dry)	66
SMR catalyst (USD_{2010}/kg)[a]	10.30
ATR catalyst (USD_{2010}/kg)[b]	10.30
Tar cracker / methane reformer catalyst (USD_{2010}/kg)[c]	51.5
DME synthesis catalyst (USD_{2010}/L DME) [d]	0.0044
Hydrocarbonylation catalyst (USD_{2010}/L ethanol)[d]	0.0044
Carbonylation catalyst (USD_{2010}/L ethanol)[d]	0.0044
Lo-Cat Chemical (USD_{2010}/kg sulfur produced)	0.15
Amine chemical and adsorbents (USD_{2010}/CO_2 tonne)	3.3
Waste water (USD_{2010}/m^3)	0.731
Boiler chemicals (USD_{2010}/tonne)	0.12
Water demineralization (USD_{2010}/tonne)	0.34
Ash disposal cost (USD_{2010}/tonne)	29.02

[a] GSHV (standard conditions) =1780 h^{-1}, 25% catalyst replacement per year, catalyst density= 910 kg/m^3

[b] assumed identical for the ATR

[c] assumed as the price of the SMR catalyst by a factor of 5

[d] assumed (no better data available)

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Curriculum Vitae

Pedro Haro was born in Sevilla (Spain) in 1986. In 2004, he began Chemical Engineering at the *Universidad de Sevilla* and, in 2007; he joined the Bioenergy Group (BEGUS) as an intern. In 2009, he obtained the Chemical Engineering long-cycle (5 years) degree (as the first in his class) and, in 2010, he obtained a predoctoral scholarship under the supervision of Prof. Ollero. In 2011, Pedro obtained an MSc (major in Environmental Engineering) and a FPU grant (Chemical Technology) from the Spanish Ministry of Education. During 2012, he visited the *Karlsruhe Institut für Technologie* (KIT) as invited PhD student, where he collaborated in the bioliq$^{®}$ project. In 2012 and 2013, he lectured Chemical Engineering at the *Universidad de Sevilla*.

Pedro’s main research areas are process design and simulation, technoeconomic and environmental sustainability assessments of thermochemical biorefineries.

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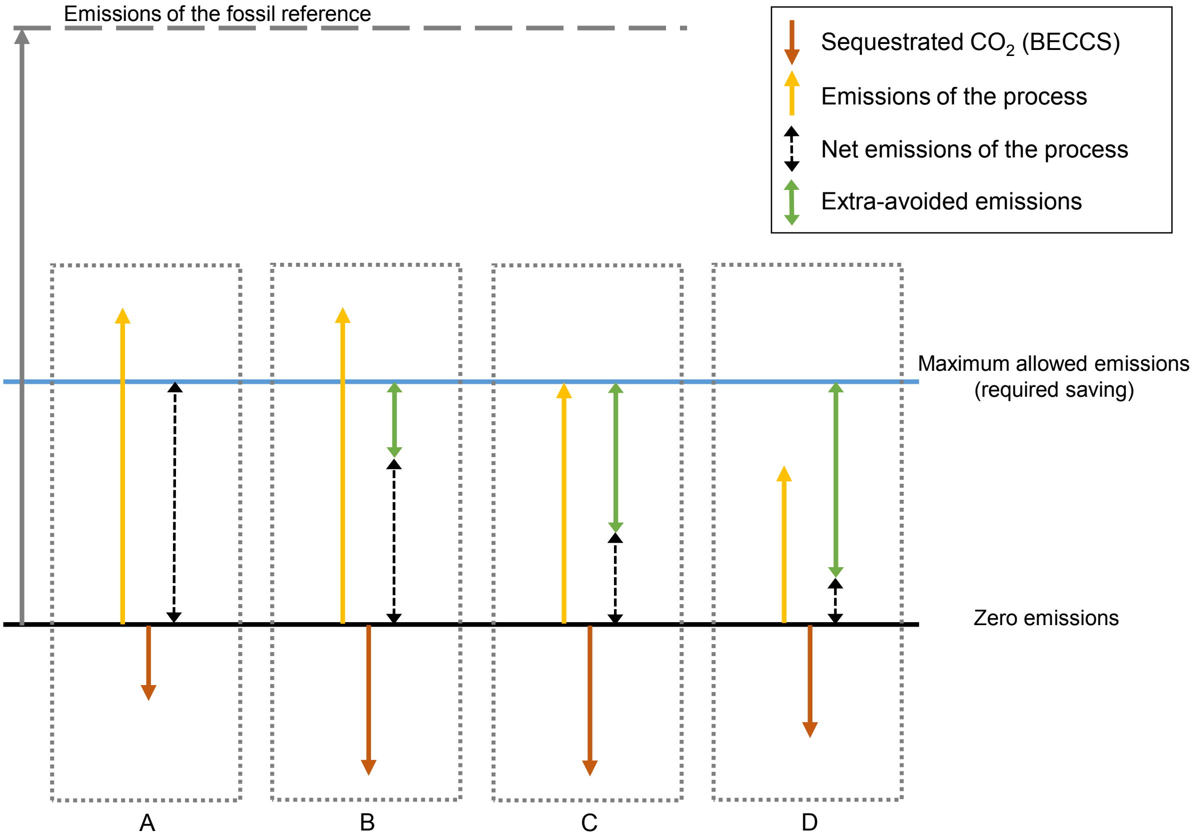
Emissions of the fossil reference
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Net emissions of the process
Extra-avoided emissions
Maximum allowed emissions (required saving)
Zero emissions
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