Thermochemical Biorefineries based on DME as platform chemical

Conceptual design and technoeconomic assessment

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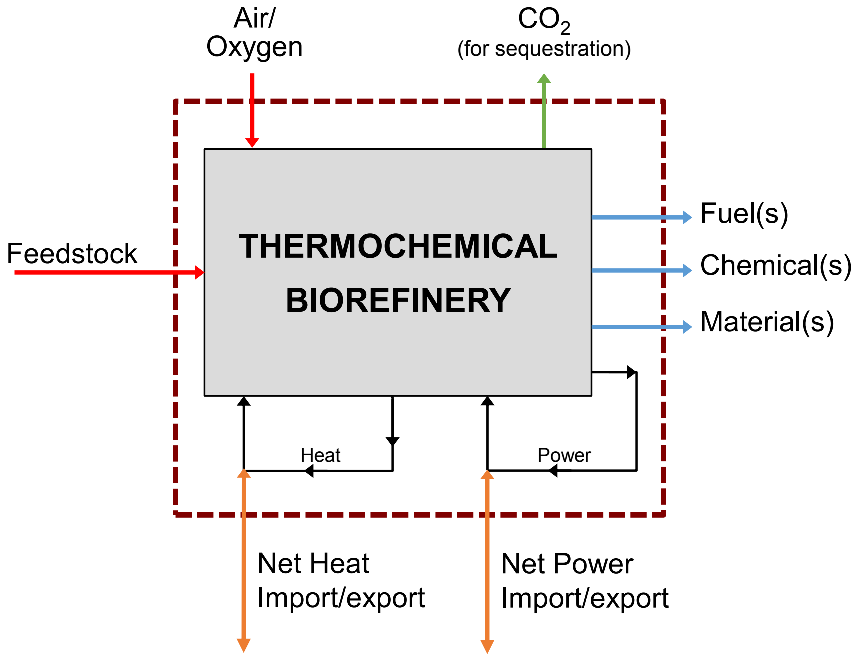
Contents

Objective

This thesis aims to propose **new concepts of thermochemical biorefineries using DME as a platform chemical** and to assess if they are **feasible, profitable and sustainable**



A thermochemical biorefinery is a facility, which processes biomass by means of pyrolysis and/or <u>gasification</u> to produce fuels, chemicals and services

History and context

In **2009**, the research activity of the **Bioenergy Group** (process design) was focused on the production of **ethanol** via **thermochemical processing** of biomass:

DIRECT SYNTHESIS

The study of the direct synthesis showed that the process is **feasible**. However,

(just) profitable and there is

a **high risk**, since large investment **400 M€ (500 MW$_{th}$)**

and **market uncertainties**

Indirect synthesis of Ethanol

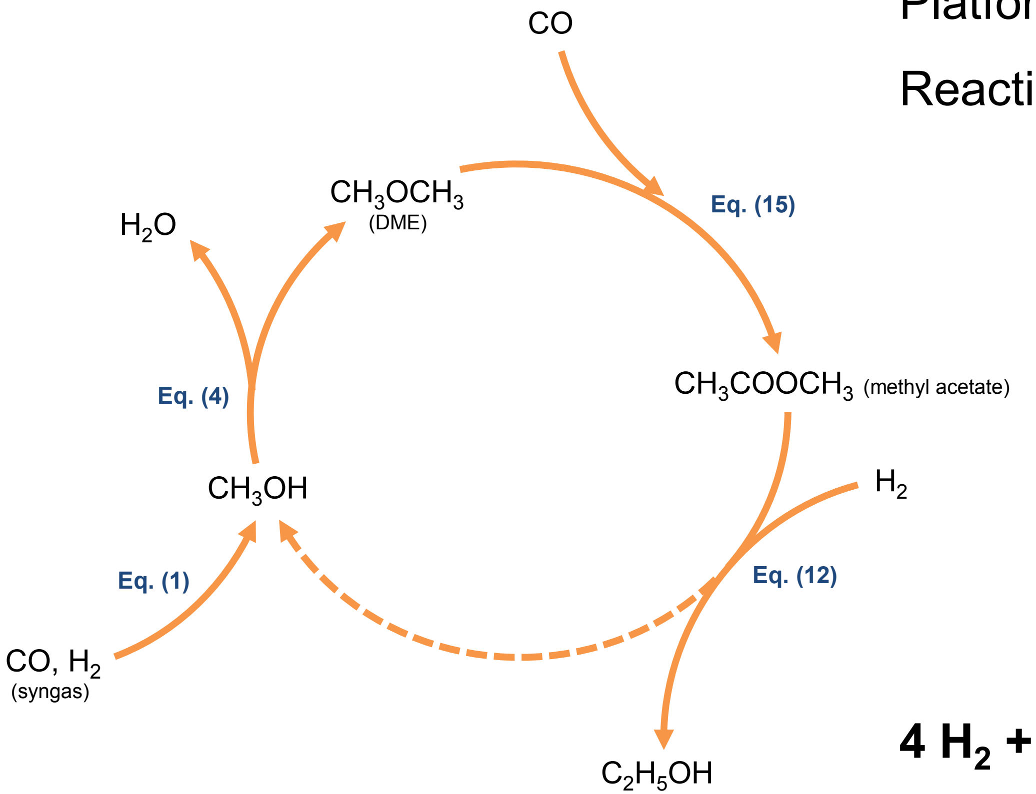
- Objective: **improve profitability**

INDIRECT SYNTHESIS

- Search of alternative routes that overcome main limitation of direct synthesis: **low selectivity to ethanol**
- The **screening** of literature showed all routes use **homogeneous catalysts** and operate at **high pressure (>50 bar)**
  - Acetic acid esterification (**Enerkem**): complex
    - In process to be commercial (homogeneous catalyst)
  - **DME hydrocarbonylation**
    - Recently discovered (2009, Tsubaki)
    - Heterogeneous catalyst

Indirect synthesis of Ethanol

❑ Selected route: **DME hydrocarbonylation**



Platform chemical**: DME**

Reaction steps:

syngas-to-methanol (commercial)

methanol-to-DME (commercial)

DME-to-ethanol (in progress)

two catalysts

220ºC, 15 bar

Methanol is converted into DME

GLOBAL REACTION:

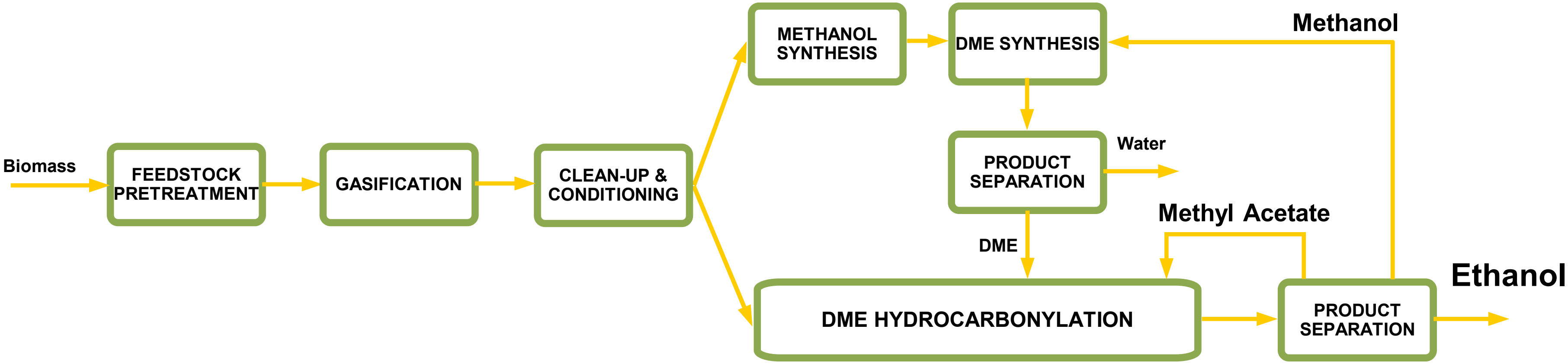
$$\mathbf{4\ H_2 + 2\ CO \rightarrow C_2H_5OH + H_2O}$$

(same as in the direct route)

Indirect synthesis of Ethanol

Paper 2

- Process design (***i-Ethanol concept***)



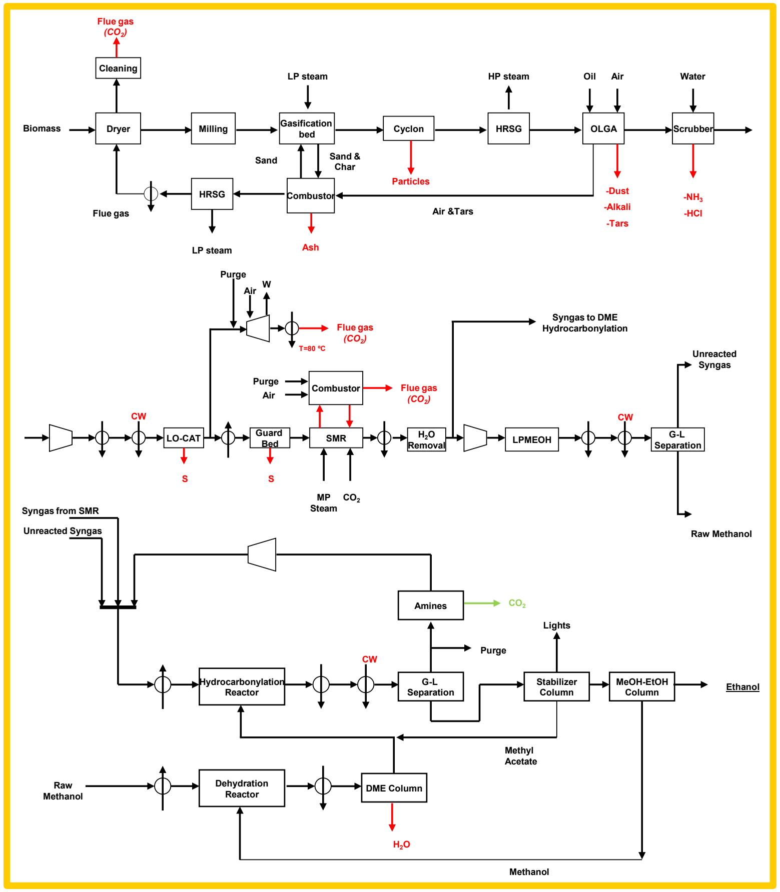
Main points in the design:

- A large excess of CO is required (**CO/DME = 10:1**)
- **Selectivity near 100%**
- **No water-ethanol** mixture (energy saving)
- **Less syngas recycle, milder operating conditions**

Indirect synthesis of Ethanol

Paper 2

❑ Basis of modeling (***i-Ethanol*** *concept*)



Process flowchart of the i-Ethanol concept

- ❑ Process simulator: **Aspen Plus**
- ❑ **500 MW$_{th}$** of poplar chips
- ❑ **i-CFB** gasifier
- ❑ Conditioning of raw syngas
  - ❑ steam reformer (SR)
- ❑ Methanol synthesis
  - ❑ **LPMEOH™**
- ❑ DME synthesis
  - ❑ **methanol dehydration** (Toyo)
- ❑ DME hydrocarbonylation
  - ❑ data from literature (Tsubaki)

Indirect synthesis of Ethanol

Paper 2

- Results and comparison with the direct route (***i-Ethanol concept***)

	i-Ethanol	Direct synthesis
Biomass input ($MW_{th,\ HHV}$)	500	500
Feedstock price ($/d. tonne)	66	66
Energy efficiency (%, HHV)	46	34
Total capital investment ($M\$_{2010}$)	333	421
Operating cost ($k\$/MW_{EthOH}\cdot year$)	435	471
Minimum selling price ($/L) [10% internal rate of return: IRR]	0.56	0.71

Data for the direct synthesis taken from BEGUS publications

Both cases share the methodology and have been designed as

energy self-sufficient

Indirect synthesis of Ethanol

- Conclusions
  - The indirect synthesis has **higher efficiency** and **higher profitability** than direct synthesis
  - However, there is still a **risk for the investment**
    - In order to reduce it: **diversification of revenue → multiproduction**
    - Regarding the **DME hydrocarbonylation route** there are **potential co-products: DME, methyl acetate (high-value)**

Multiproduction plants using a platform chemical

Paper 5

- ❑ Design and assessment of 12 concepts of thermochemical biorefineries
  - ❑ Objective: **confirm the potential of multiproduction plants**
  - ❑ How?
    - ❑ Assessment of **different configurations** (concepts) regarding **the mix of products** and the **conditioning of the syngas**

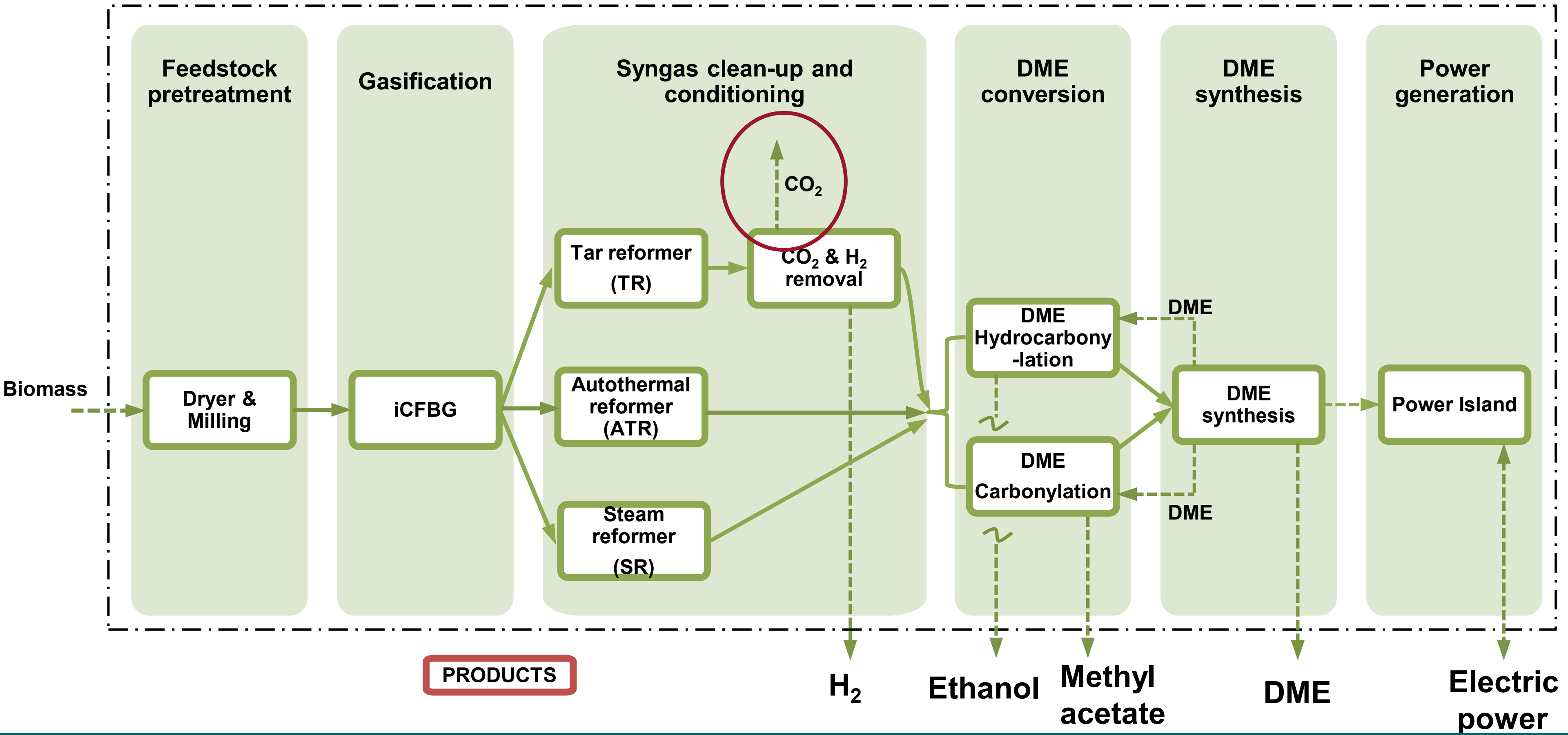
Co-products	Uses	Value	€/GJ
DME	substitute of diesel, LPG; substitute of naphtha (chemical)	**0.7 $/L**	**22**
Ethanol	substitute of gasoline; production of chemicals (butanol, ethylene)	**0.6 $/L**	**24**
Methyl Acetate	solvent; production of plastics	**1.7 $/L**	**65**
Hydrogen	production of electricity; use in transport; refineries	**1 $/kg**	**6**
Electricity	-	**5 c$/kWh**	**-**

Multiproduction plants using a platform chemical

Paper 5

❑ Description of the concepts

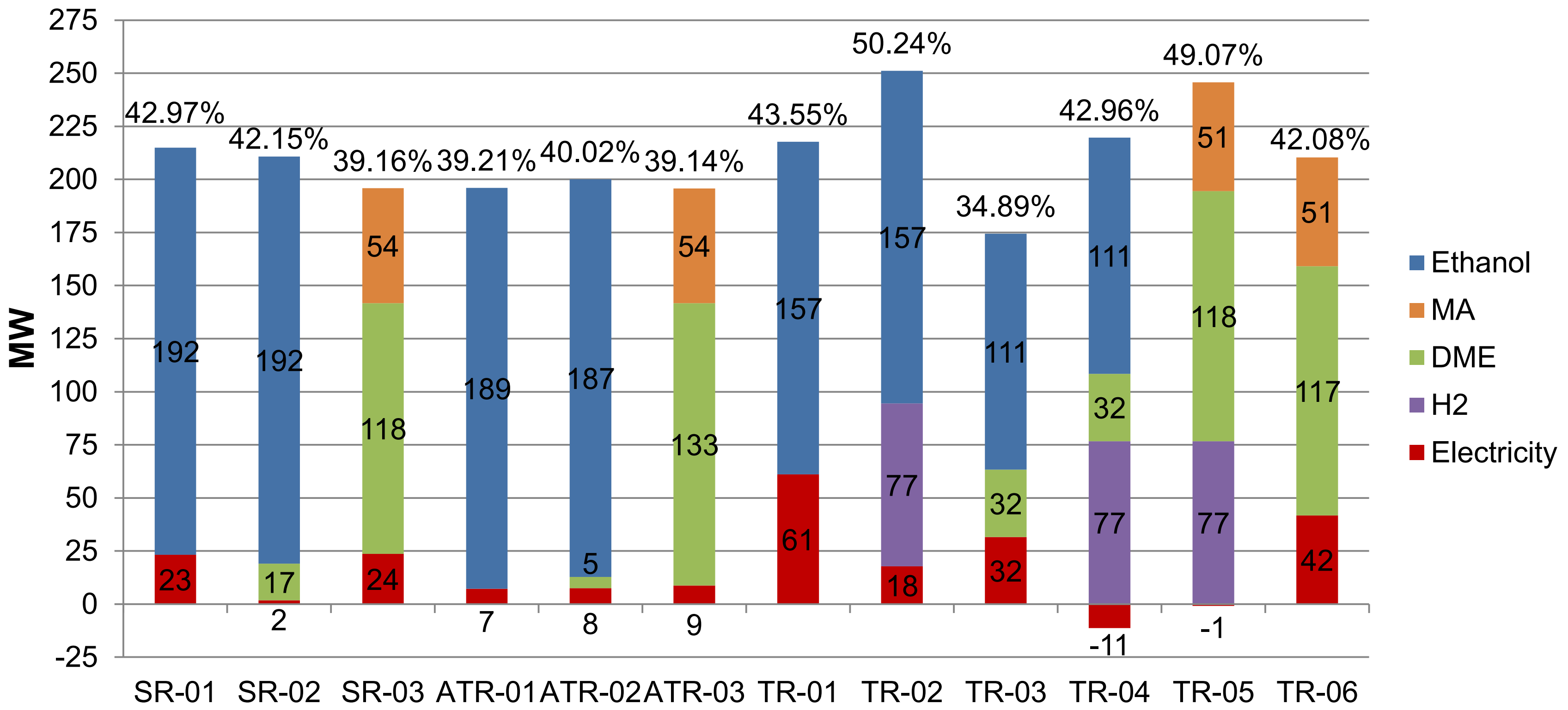
Process flowchart of the concepts of thermochemical biorefinery



Multiproduction plants using a platform chemical

❑ Results and discussion

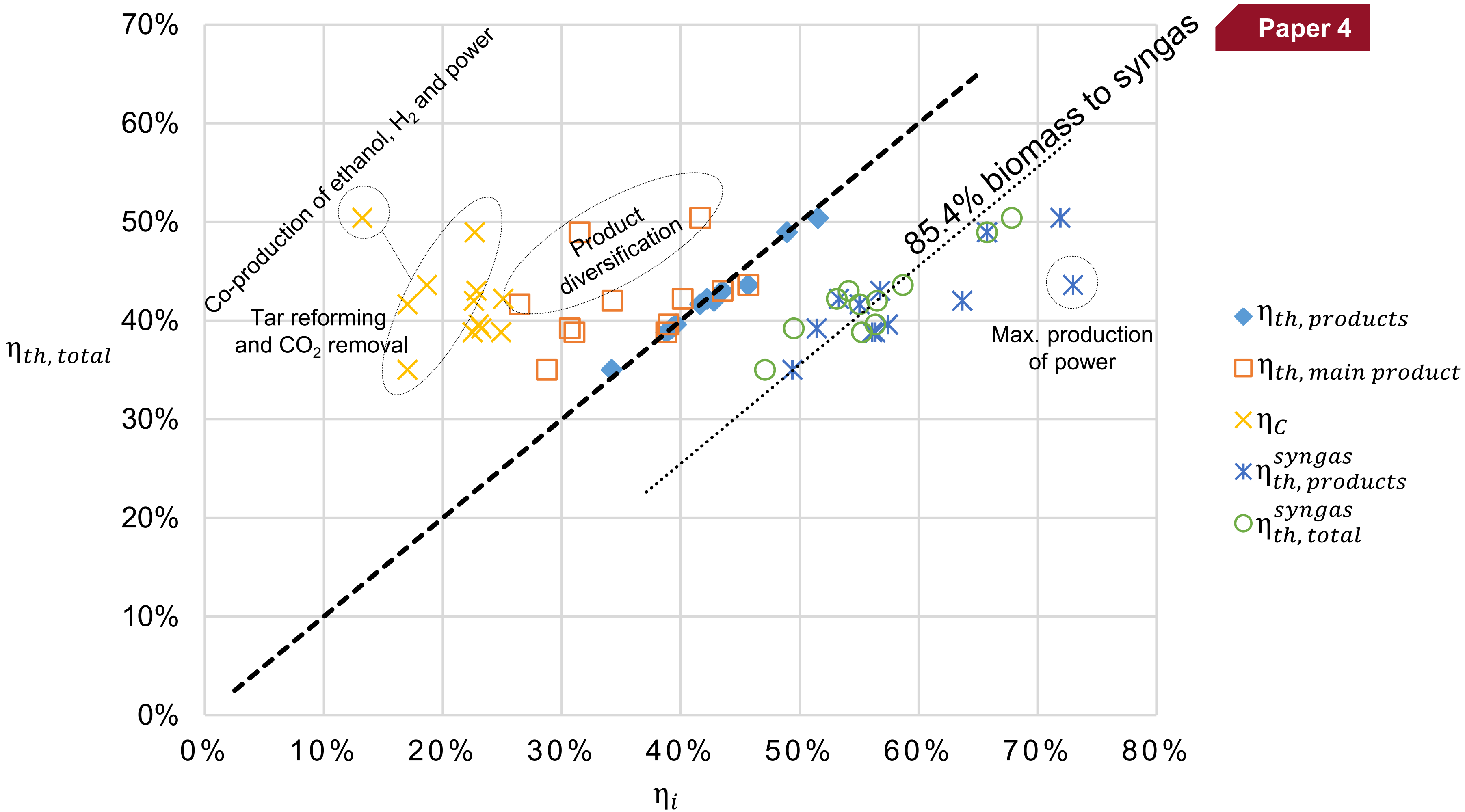
Paper 5



Energy efficiency of the concepts

Multiproduction plants using a platform chemical

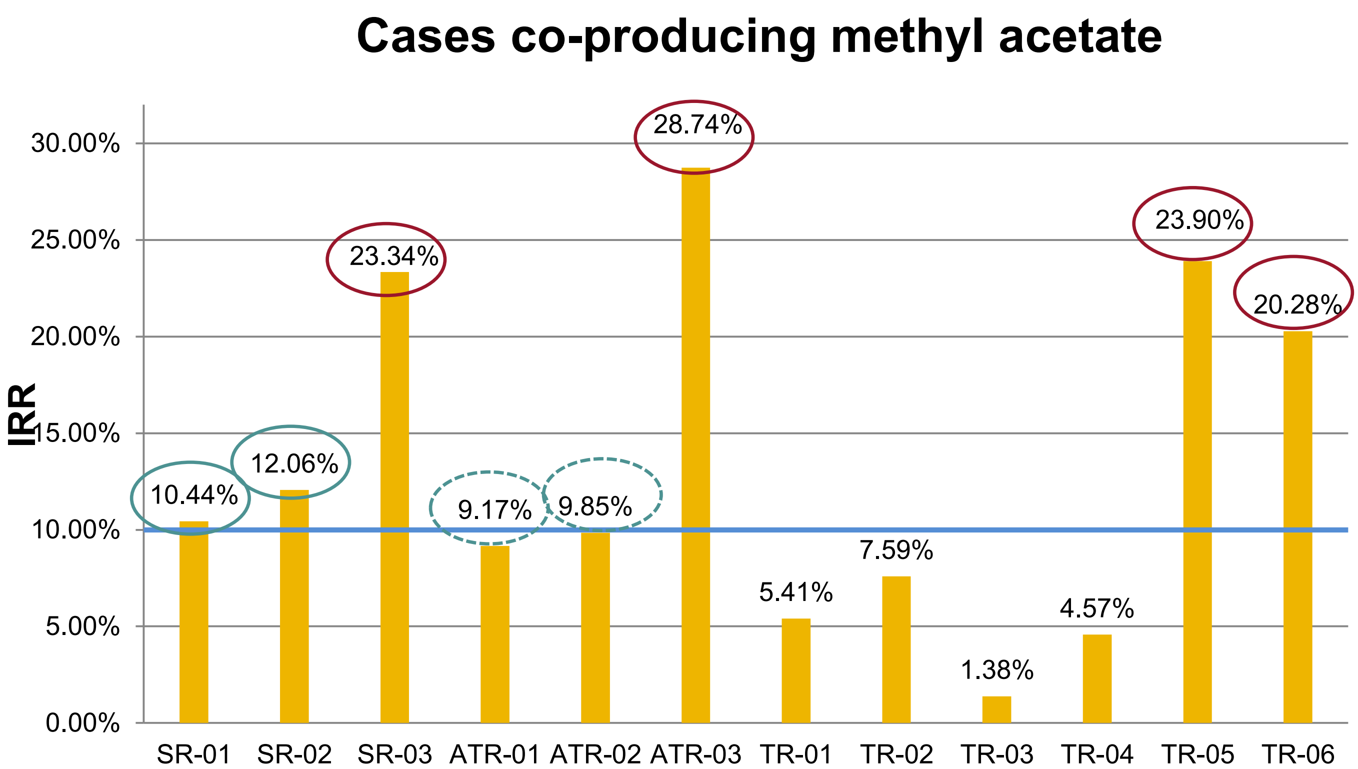
Paper 4



Multiproduction plants using a platform chemical

- Results and discussion

Paper 5



IRR of the concepts

Multiproduction plants using a platform chemical

- Conclusions
  - The concepts co-producing **methyl acetate** (high-value product) achieve the **highest profitability**
  - The energy efficiency of the concepts is similar to BTL/G processes (40%)
- **However, a sustainability assessment is necessary**

Sustainability in multiproduction plants

- **Sustainability assessment** in thermochemical biorefineries
  - The use of biomass does not necessarily involve sustainability
  - The co-production of products different to fuels requires **new tools**
- **Impact** of sustainability on the **profitability**
  - The incorporation of **BECCS** (sale of CO_2 credits)
  - Achievement of a **larger saving** than the required (sale of CO_2 credits)

Assessment of **sustainability (new methodology)** and

study of the potential **impact** on **profitability**

(based on Directive 2009/28/EC)

Sustainability in multiproduction plants

- European methodology **Paper 7**
  - $E = e_{ec} + e_l + e_p + e_{td} + e_u - e_{sca} - e_{ccs} - e_{ccr} - e_{ee}$
    (g CO_2 equivalent / MJ of biofuel)
  - Allocation co-products (energy content):
    $E_m = E' + sum[x_i \cdot (e_{td,i} + e_{u,i})]$
- Modification of sustainability methodology
  - The final use ($e_{u,i}$) is relevant
    - **Fuels** have a **net emission** in their final use
    - **Retention** of carbon in **chemicals**
      (assumed as 50% eq. CO_2 content)
  - **Extra saving**

Example: TR-01 concept

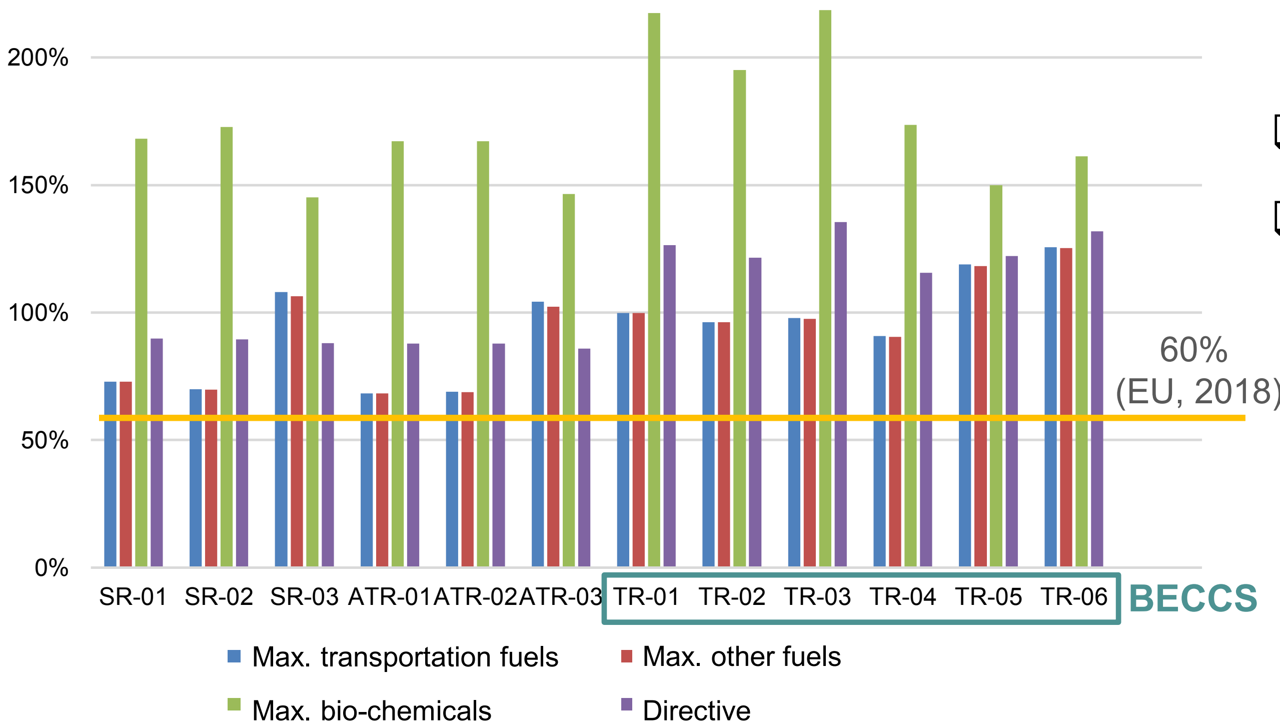
Emission factor (fossil)	**83.8**	g CO_2 equivalent per MJ of total products
Limit of emissions (60% saving)	33.5	
Emissions cradle-to-grave	9.0	
Sequestration or retention of CO_2	30.0	
Saving	***125%***	
Extra saving (w/o seq. or retention of CO_2)	24.5	
Extra saving	**54.5**	

- **Extra-avoided emissions: 44.3 t/h of equivalent CO_2**

Sustainability in multiproduction plants

- Results: final use and extra saving

Paper 7



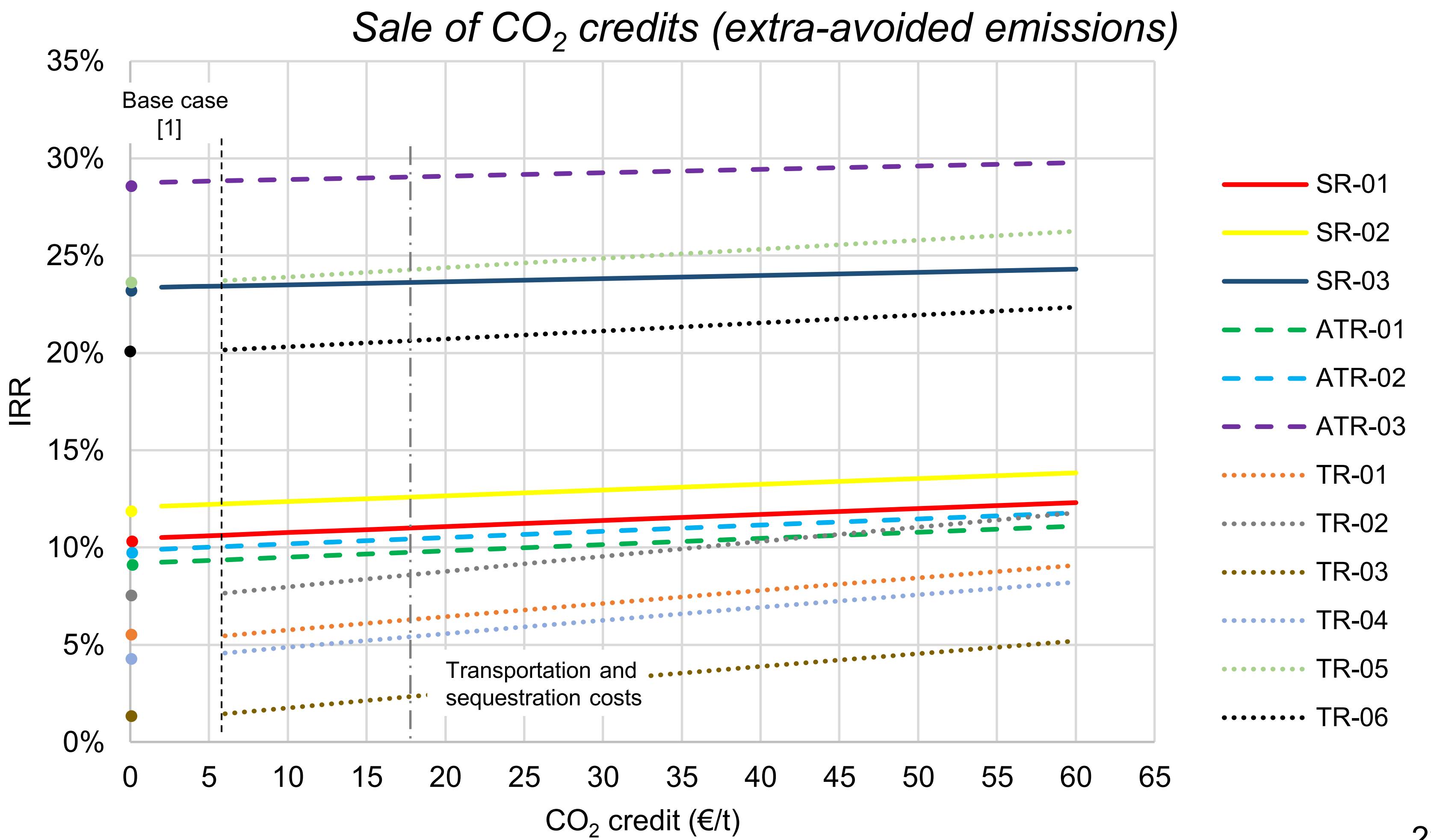
Saving of GHG emissions (%)

- Directive (EU)
- Final use:
  - As transportation fuels
  - As chemicals

Sustainability in multiproduction plants

- **BECCS**: results of incorporation to TR concepts
  - Cost of sequestration: 20 – 30 €/tonne
  - Conventional power plants: 100 – 200 €/tonne
- All concepts have an extra saving of GHG emissions
  - **Impact of sustainability on profitability**
    - Sale of CO_2 credits (extra-avoided emissions)
    - Co-feeding of fossil fuels (natural gas, coal)

Sustainability in multiproduction plants



Sustainability in multiproduction plants

Co-feeding of fossil fuels: *SR-01*	
Extra saving	25.2 g/MJ
Co-feeding (coal)	**49 MW**
Increment of IRR	**10.44 → 11.24 %**

Co-feeding results in the largest profitability

when CO_2 credit < 20 €/tonne

Sustainability in multiproduction plants

- Conclusions

Paper 7

- **All concepts** of thermochemical biorefinery using DME are **sustainable** (even using European regulation)
- Chemicals are not combusted → **retention of carbon**
- A saving larger than 100% could be achieved if chemicals are co-produced and BECCS incorporated
- The economic impact is positive due to the large GHG saving

Thermochemical biorefineries with multiproduction

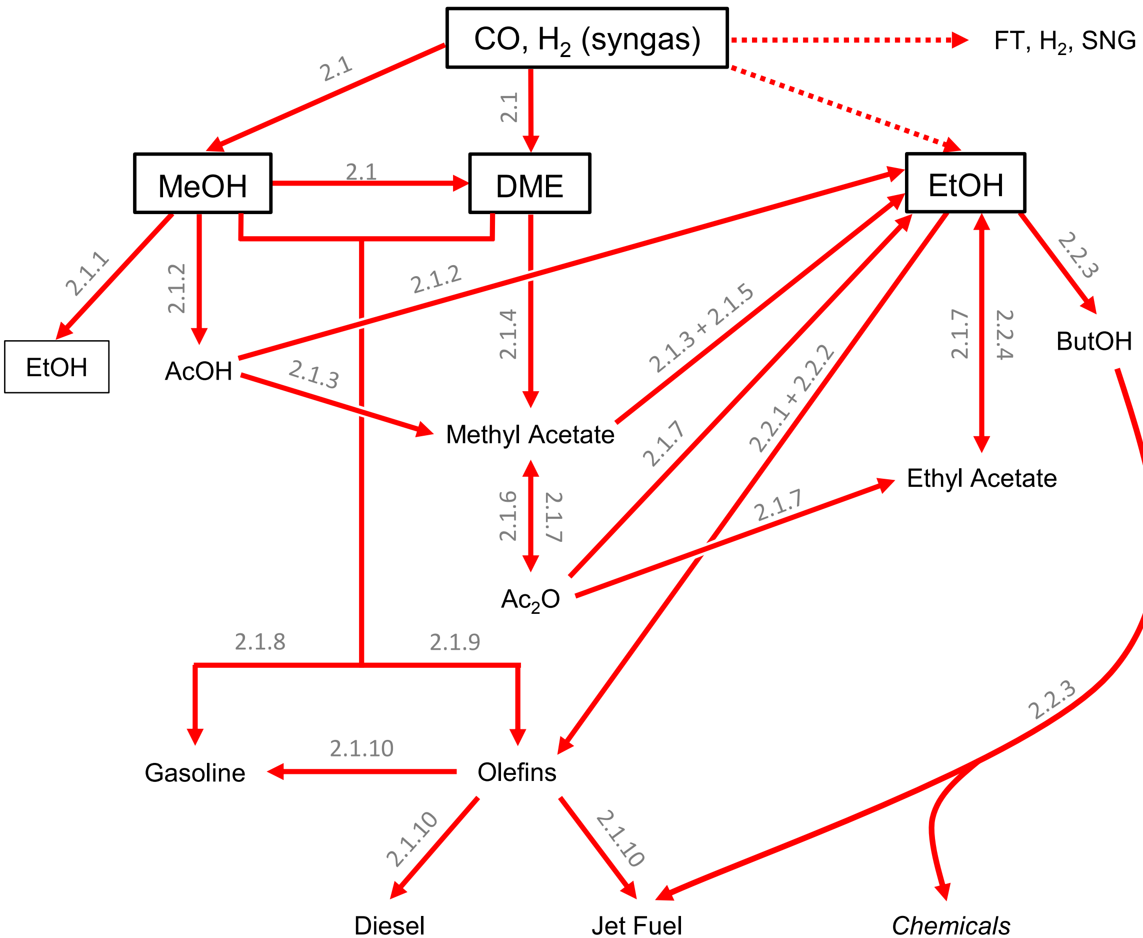
- Up to now the results have shown that:
  - **Multiproduction is interesting in order to reduce the risk (diversification of revenue) and enhances profitability**

- Hence, a **review of other platform chemicals and indirect routes** will result in **new options for** the assessment of **multiproduction plants**

Identification of chemical routes using a platform chemical

Paper 1

- Platform chemicals (from syngas) for thermochemical biorefineries



- Methanol, DME and Ethanol
- Methanol and DME are mostly equivalent
- The routes are complex (several reaction steps)
- **MTG** and **MTO** are commercial processes, although using fossil fuels

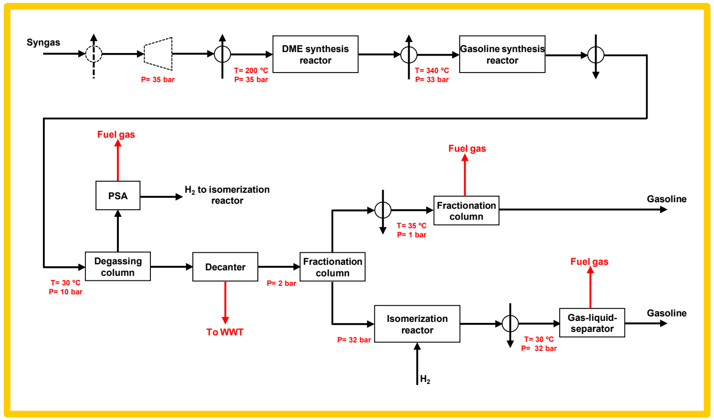
Activities during the visit to KIT

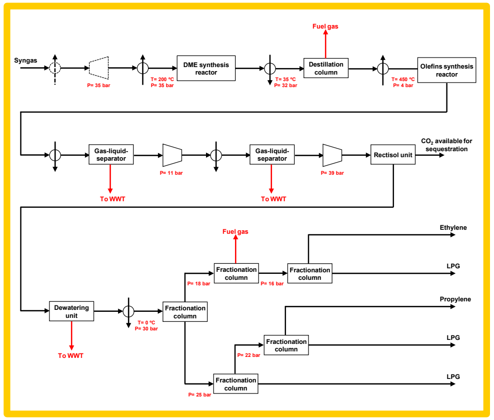
- ❑ In 2012 I visited the Karlsruhe Institute of Technology

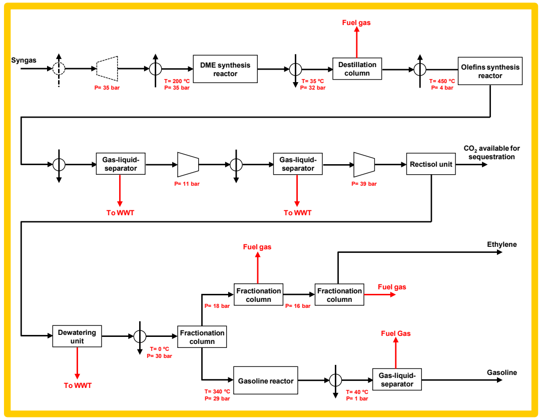
  - ❑ **As a result of this collaboration**:

Paper 6

- ❑ Modeling and assessment of the production of **synthetic gasoline**, **olefins** and **co-production of synthetic gasoline and ethylene**







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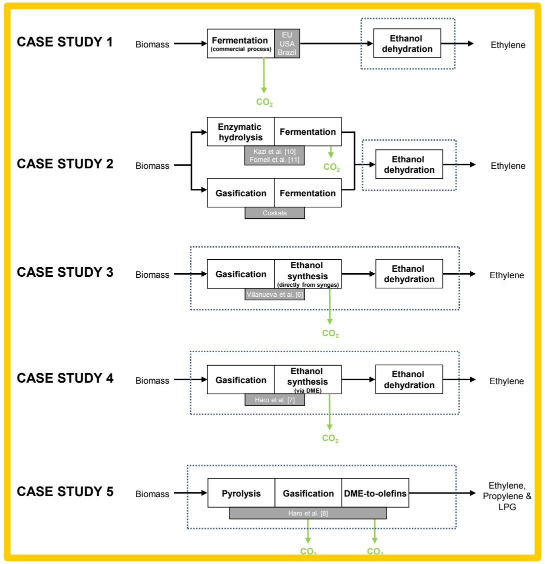
Paper 3 ❑ Assessment of the production of **ethylene** using **DME and/or ethanol** as a platform chemical



Activities during the visit to KIT

- In 2012 I visited the Karlsruhe Institute of Technology
  - **As a result of this collaboration**:
    - Paper 6 — Modeling and assessment of the production of **synthetic gasoline**, **olefins** and **co-production of synthetic gasoline and ethylene**
    - Paper 3 — Assessment of the production of **ethylene** using **DME and/or ethanol** as a platform chemical
  - **Main differences with the previous work (BEGUS)**
    - Different gasification technology (EF)
    - Different methodology and basis of design (e.g. 1175 MW_{th} straw)
  - Hence, a comparison of the concepts is not possible

Activities during the visit to KIT

- Results

Papers 3 and 6

- The production of **synthetic gasoline and olefins** (2 concepts) are **not competitive**
- Production of **ethylene** using ethanol as a platform chemical
  - **Competitive** for sugar cane ethanol **(Brazil)**
  - **Competitive** for ethanol via thermochemical processing **(indirect synthesis)**

Ethanol price 0.45 €/L

Summary (thesis)

- 20 concepts of thermochemical biorefineries (designed and assessed)
  - Most concepts use **DME as a platform chemical** (17); the rest ethanol (3)
  - **Multiproduction plants** (14) are designed with regarding different reforming technologies and different co-products
  - The list of co-products includes:
    - Fuels (transportation, heating), commodities (low-value) and chemicals (high-value)

Summary (thesis)

- Summary of the thesis (work done)

Paper 1	Identification of chemical routes using a platform chemical
Paper 2	Technoeconomic assessment of the indirect synthesis of ethanol
Paper 3	Technoeconomic assessment of the production of ethylene
Paper 4	Conceptual design of multiproduction plants
Papers 5 and 6	Technoeconomic assessment of multiproduction plants using DME
Paper 7	Assessment of sustainability and economic impact

Final Conclusions

- **Ethanol** can be produced via the **DME hydrocarbonylation** route**:**

  cost-competitive and high efficient (0.56 $/L)

- **Multiproduction** can **reduce** the **risk** of investment and **improve profitability:**

  especially high-value chemicals (IRR > 20 %)

- Co-production of **chemicals** largely **reduces** the **GHG emissions**

  retention of carbon in final products

- **Extra saving** in thermochemical biorefineries enhances profitability

  sale of CO_2 credits or co-feeding

- **BECCS** is **competitive** and enhances profitability

  lower cost of sequestration (20-30 €/tonne)

Further work

Experimental research of DME hydrocarbonylation route:

1.- Optimization of operating conditions

2.- Design of reactor (e.g. regeneration of catalyst)

Assessment of other **routes** using DME and others platform chemicals and the **screening** of other **high-value chemicals (currently used in petrochemical industry)**

Thank you for your attention!

¡Gracias por vuestra atención!