## Thermochemical Biorefineries based on DME as platform chemical

#### Conceptual design and technoeconomic assessment

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Seville, June 24th 2013

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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

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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<sub>th</sub>) 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



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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

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#### Indirect synthesis of Ethanol

Paper 2

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Basis of modeling

#### (i-Ethanol concept)



Process flowchart of the i-Ethanol concept

- □ Process simulator: Aspen Plus
- □ **500 MW**<sub>th</sub> of poplar chips
- □ i-CFB gasifier
- □ Conditioning of raw syngas
  - □ steam reformer (SR)
- Methanol synthesis

□ LPMEOH<sup>™</sup>

- DME synthesis
  - methanol dehydration (Toyo)
- DME hydrocarbonylation

□ data from literature (Tsubaki)

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#### Indirect synthesis of Ethanol

Paper 2 Results and comparison with the direct route (*i-Ethanol concept*)

	i-Ethanol	Direct synthesis
Biomass input (MW <sub>th, HHV</sub> )	500	500
Feedstock price (\$/d. tonne)	66	66
Energy efficiency (%, HHV)	46	34
Total capital investment (M\$ <sub>2010</sub> )	333	421
Operating cost (k\$/MW <sub>EthOH</sub> ·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

Seville June 24<sup>th</sup> 2013 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** 
  - $\Box$  In order to reduce it: diversification of revenue  $\rightarrow$

#### multiproduction

Regarding the DME hydrocarbonylation route there are potential co-products: DME, methyl acetate (high-value)



Paper 5 Design and assessment of 12 concepts of thermochemical biorefineries				
Objective: confirm the potential of multiproduction plants				
[	⊐ How?			
	Assessment of different configuration	ns (conce	epts)	
regarding the mix of products and the conditioning of				
	the syngas			
Co-products	Uses	Value	€/GJ	

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	-
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#### Paper 5 Description of the concepts

Process flowchart of the concepts of thermochemical biorefinery

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Results and discussion

Paper 5



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ERSIDAD



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Results and discussion



#### Cases co-producing methyl acetate



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#### 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 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

- $\Box$  The incorporation of **BECCS** (sale of CO<sub>2</sub> credits)
- $\Box$  Achievement of a larger saving than the required (sale of CO<sub>2</sub> credits)

### Assessment of **sustainability (new methodology)** and study of the potential **impact** on **profitability** (based on Directive 2009/28/EC)



European methodology

Paper 7

$$\Box E = e_{ec} + e_{l} + e_{p} + e_{td} + e_{u} - e_{sca} - e_{ccs} - e_{ccr} - e_{ee}$$

(g CO<sub>2</sub> equivalent / MJ of biofuel)

□ Allocation co-products (energy content):

$$\mathsf{E}_{\mathsf{m}} = \mathsf{E}' + \mathsf{sum}[\mathsf{x}_{\mathsf{i}} \cdot (\mathsf{e}_{\mathsf{td},\mathsf{i}} + \mathsf{e}_{\mathsf{u},\mathsf{i}})]$$

□ Modification of sustainability methodology

 $\Box$  The final use (e<sub>u,i</sub>) is relevant

□ Fuels have a net emission in their final use

□ Retention of carbon in chemicals

(assumed as 50% eq. CO<sub>2</sub> content)

Extra saving

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#### Example: TR-01 concept

Emission factor (fossil) Limit of emissions (60% saving)	<b>83.8</b> 33.5	
Emissions cradle-to-grave	9.0	a CO <sub>2</sub> equivalent per MJ of total produc
Sequestration or retention of CO <sub>2</sub>	30.0	
Saving	125%	9 2 - 4 p
Extra saving (w/o seq. or retention of CO <sub>2</sub> )	24.5	
Extra saving	54.5	
Extra avoided emissions: 44.3 t/b of equivalent CO		

Extra-avoided emissions: 44.3 t/n of equivalent  $CO_2$ 

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□ Results: final use and extra saving

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□ **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<sub>2</sub> credits (extra-avoided emissions)

□ Co-feeding of fossil fuels (natural gas, coal)



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

**Co-feeding results in the largest profitability** 

when CO<sub>2</sub> credit < 20 €/tonne

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Conclusions

Paper 7

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

□ 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

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Identification of chemical routes using a platform chemical

□ Platform chemicals (from syngas) for thermochemical biorefineries



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Paper 1



Activities during the visit to KIT

□ In 2012 I visited the Karlsruhe Institute of Technology

□ As a result of this collaboration:

Paper 6 Define and assessment of the production of synthetic gasoline, olefins and co-production of synthetic gasoline and ethylene



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## Activities during the visit to KIT

□ In 2012 I visited the Karlsruhe Institute of Technology

#### □ As a result of this collaboration:

- Paper 6 Define and assessment of the production of synthetic gasoline, olefins and co-production of synthetic gasoline and ethylene
  - Assessment of the production of ethylene using DME and/or

ethanol as a platform chemical



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Paper 3

#### Activities during the visit to KIT

In 2012 I visited the Karlsruhe Institute of Technology

#### □ As a result of this collaboration:

- Paper 6 Define 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<sub>th</sub> straw)
  - □ Hence, a comparison of the concepts is not possible



□ 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)



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**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<sub>2</sub> credits or co-feeding

□ BECCS is competitive and enhances profitability

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

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#### **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!

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