A Short Review on 2nd Generation Processes to Produce Ethanol from Biomass

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Outline

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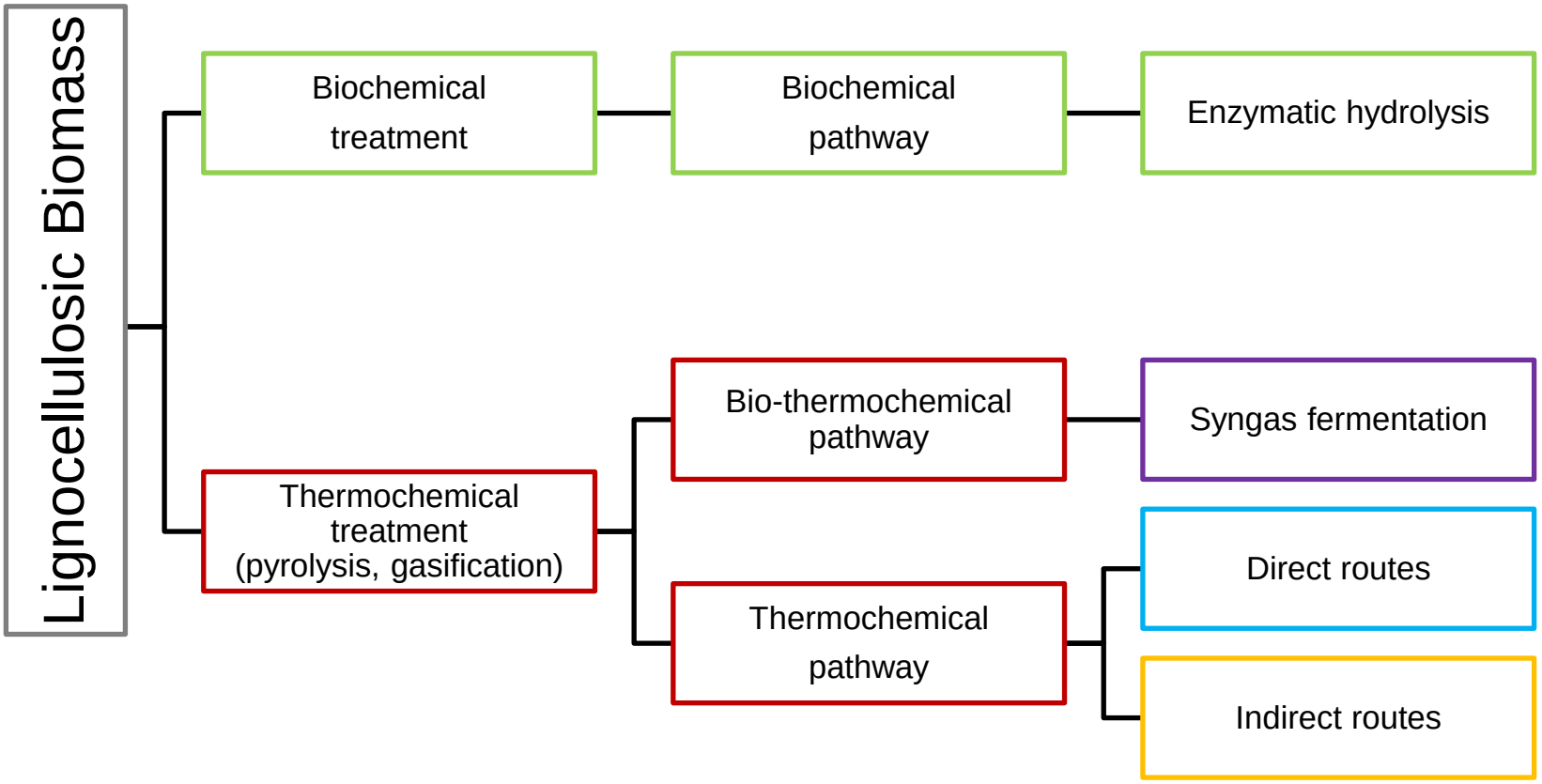

Biochemical pathway

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Strengths:

- **Simple process (in comparison)**
- **Non-thermal treatment**
- **Widely investigated**

Weaknesses:

- **Price of enzymes (enzymatic hydrolysis)**
- **Need of genetic improvements**
- **Conversion of lignin**

Bio-thermochemical pathway

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Strengths:

- **High specificity to ethanol production**
- **Independent of mild changes of H_2/CO ratio**
- **Poison-tolerant (S)**

Weaknesses:

- **Mass transfer limitation**
- **Exhaustive control of pH and T**
- **Duality of acetogenesis/solvatogenesis cycles**

Thermochemical pathway

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Strengths:

- **Ethanol recovery (higher ethanol concentration)**
- **Use of industrial catalysts and processes**

Weaknesses:

- **Catalyst (selective, process conditions, …)**
- **Valorization of sub-products**

Thermochemical pathway

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DIRECT ROUTES

* Villanueva Perales AL, Reyes Valle C, Ollero P, Gómez-Barea A. Technoeconomic assessment of ethanol production via thermochemical conversion of biomass by entrained flow gasification. Energy 2011;36:4097e108.

- **Heterogeneous catalyst**
  - **FT-modified**
  - **MeOH-modified**
  - **Mo (S_2Mo)**
  - **Rh**

- **Low ethanol yield**
- **High subproduct formation (CO_2, CH_4, methanol, …)**

Little improvements are expected in the future

Thermochemical pathway

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INDIRECT ROUTES

- **Started in the 80's (withdrawn, but recently recovered)**
  - **Homogeneous catalyst (similar to acetic acid production)**
  - **Heterogeneous catalyst (new processes)**
  - **Need of intermediate(s) → Complex routes**
  - **Lower by-product formation, higher ethanol yields**

An old field with promising future

Indirect routes

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- Methanol homologation
- Acetic acid hydrogenation
- Acetic acid esterification
- DME hydrocarbonylation
- Acetic anhydride route
- Ethylene hydration

SYNGAS

- Thermochemical processing, e.g. biomass gasification

MeOH

- Methanol synthesis (well-known process)

$$CO + 2\,H_2 \rightarrow CH_3OH$$

EtOH

- **Methanol homologation (reductive carbonylation)**

$$CH_3OH + CO + 2\,H_2 \rightarrow C_2H_5OH + \boldsymbol{H_2O}$$

$$CH_3OH + 2\,CO + H_2 \rightarrow C_2H_5OH + \boldsymbol{CO_2}$$

Homogeneous catalyst (similar to acetic acid synthesis)

No current commercial process
Argonne National Laboratory

Indirect routes

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SYNGAS

- Thermochemical processing, e.g. biomass gasification

MeOH

- Methanol synthesis (well-known process)

$$CO + 2\,H_2 \rightarrow CH_3OH$$

AcOH

- **Methanol carbonylation**

$$CH_3OH + CO \rightarrow CH_3COOH$$

Monsanto/Cativa process (homogeneous catalyst)

EtOH

- **Acetic Acid Hydrogenation**

$$CH_3COOH + 2\,H_2 \rightarrow C_2H_5OH + H_2O$$

Heterogeneous catalyst, corrosiveness process

No current commercial process
ENSOL (80's)
BP, Celanese, Range Fuels (today)

Indirect routes

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SYNGAS

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MeOH

- Methanol synthesis (well-known process)

$$CO + 2\,H_2 \rightarrow CH_3OH$$

MeOAc

- **Acid carbonylation of methanol & Acetic acid esterification**

$$2\,CH_3OH + CO \rightarrow CH_3COOCH_3 + H_2O$$

$$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$$

EtOH

- **Hydrogenation of methyl acetate**

$$CH_3COOCH_3 + 2H_2 \rightarrow C_2H_5OH + CH_3OH$$

- Heterogeneous catalyst, mild pressure, selective reaction

Near to be commercial
Enerkem Inc.
(2-3 pre-commercial plants in USA and Canada)

Indirect routes

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- Acetic anhydride route
- Ethylene hydration

SYNGAS

- Thermochemical processing, e.g. biomass gasification

MeOH

- Methanol synthesis (well-known process)

$$CO + 2\,H_2 \rightarrow CH_3OH$$

DME

- **Methanol dehydration (commercial)**

$$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

EtOH

- **DME hydrocarbonylation (in development)**

$$CH_3OCH_3 + CO + 2\,H_2 \rightarrow C_2H_5OH + CH_3OH$$

- Carbonylation: H-Mordenite; Hydrogenation: Cu-ZnO
- High selective reaction operating at 200-250ºC and 15 bar

* Haro et al., Technoeconomic assessment of lignocellulosic ethanol production via dimethyl ether hydrocarbonylation, Energy 2012. doi: 10.1016/j.energy.2012.05.004

Indirect routes

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- **Methanol homologation**
- **Acetic acid hydrogenation**
- **Acetic acid esterification**
- **DME hydrocarbonylation**
- **Acetic anhydride route**
- **Ethylene hydration**

SYNGAS

- Thermochemical processing, e.g. biomass gasification

MeOH

- Methanol synthesis (well-known process)

$$CO + 2\,H_2 \rightarrow CH_3OH$$

AcOH

- **Methanol esterification**

$$CH_3COOH + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$$

EtOH

- **Methyl acetate carbonylation, esterification and hydrogenation**

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

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

$$CH_3COOCH_2CH_3 + 2H_2 \rightarrow 2\,C_2H_5OH$$

Most complex route
Halcon SD Group

Indirect routes

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- Methanol homologation
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- Ethylene hydration

SYNGAS

- Thermochemical processing, e.g. biomass gasification

MeOH

- Methanol synthesis (well-known process)

$$CO + 2\,H_2 \rightarrow CH_3OH$$

C_2H_4

- **Methanol to olefins (MTO) [high-ethylene mode]**

$$CH_3OH \rightarrow C_2H_4 + (\ldots) + H_2O$$

Commercial process (Hydro-UOP)

EtOH

- **Ethylene hydration**

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

Unprofitable with present ethylene price
Range Fuels

Thermochemical Biorefineries

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- **Integrated processes to transform biomass into equivalent products than produced in conventional *fossil* refineries**

- **A multi-product assessment (DME hydrocarbonylation) shows that ethanol can be produced at competitive prices***

*** Haro et al., Thermochemical biorefinery based on dimethyl ether as intermediate: Technoeconomic assessment. Submitted for publication, 2012.**

Conclusions/Perspectives

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- **Up to date no 2nd Generation process has demonstrated a cost-competitive ethanol production**
- **Biochemical pathway is overcome (lignin conversion)**
- **Bio-thermochemical pathway need further research**
- **Direct routes have a limited improvement**
- **Indirect routes have a high potential for medium term (Enerkem, DME hydrocarbonylation)**
- **Indirect routes fit perfectly in the thermochemical biorefinery concept**

Thank you for your attention