Synthesis and Optimization of biofuel production processes

20th April 2011
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Overview

Introduction
Energy in the world
Biofuels: Raw materials and Processes

Approach to process synthesis
Method
i.e. Bioethanol from corn (1st generation)

Results
Switchgrass as raw material
Bioethanol from switchgrass (2nd generation)
   Via hydrolysis
   Via gasification
Hydrogen from switchgrass
FT diesel from switchgrass

Biodiesel
From algae
From cooking oil

Conclusions
Introduction

Energy in the world: Contribution of renewables[1]

[1] BP annual report 2010
Introduction

Energy in the world: Contribution of renewables

Shares of world primary energy

[Graph showing the shares of world primary energy by Oil, Coal, Gas, Hydro, Nuclear, and Renewables from 1970 to 2030.]

Contributions to growth

[Bar chart showing contributions to growth from 1970 to 2030 for Renewables*, Hydro, Nuclear, Gas, Coal, and Oil.]

[1] BP annual report 2010
Energy in the world: Contribution of renewables

Only biomass provides a short term source of fuels for the transportation sector.
Current ethanol from sugar cane or corn and biodiesel from vegetable oils compete with the **food market**.

Governmental policies support the production of **lignocellulosic based biofuels and the reuse of wastes and new sources (algae)**.
Governmental policies support the production of 2nd generation of biofuels based on the high yields from crop to fuel

There is a need for optimized production processes of bioethanol, biodiesel and other fuels from lignocellulosic materials and wastes
We use mathematical programming techniques to accomplish the synthesis of the production of:

- bioethanol, FT-diesel and hydrogen, from Switchgrass,
- biodiesel from cooking oil or algae oil.
Introduction

The main concerns in biofuel industry are energy and water consumption [2, 3, 4].

Introduction

The main concern in biofuels industry is the energy efficiency of the biofuel.

Corn ethanol was deemed to consume more energy to be produced than the one it could generate, [2]

<table>
<thead>
<tr>
<th>Author (year)</th>
<th>Energy consumption/J-L⁻¹ (Btu·gal⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pimentel (2001) [34]</td>
<td>209.25×10⁵ (75118)</td>
</tr>
<tr>
<td>Keeney and DeLuca (1992) [35]</td>
<td>135.02×10⁵ (48470)</td>
</tr>
<tr>
<td>Wang et al. (1999) [36]</td>
<td>113.79×10⁵ (40850)</td>
</tr>
<tr>
<td>Shapouri et al. (2002) [7]</td>
<td>144.24×10⁵ (51779)</td>
</tr>
<tr>
<td>Wang et al. (2007) [37]</td>
<td>106.75×10⁵ (38323)</td>
</tr>
</tbody>
</table>

Energy consumption optimization is quite straightforward due to the high cost of energy

Water consumption has become a major concern in process industry due to the increase in the demand as a result of the growth of population and development around the world [5,6].

Two-thirds of the world population will face water stress by year 2025.


Introduction

Water consumption in corn ethanol plants [7]:
From 3 to 15 gal water/gal ethanol
The best possible value 2.85 gal water/gal ethanol
Mean industrial value 3.4 gal water/gal ethanol

If we use lignocellulosic raw materials [7]
6 to 9.8 gal water/gal ethanol for switchgrass
1.94-2 gal water/gal ethanol for hybrid poplar

Biodiesel production requires [8]
1 to 3 gal water/gal biodiesel

The low price of water makes it difficult to take into account in a cost function

We propose a two stage method [2] for the optimization of both:

1. **Energy optimization**  Superstructure and parameter optimization including economic evaluation to select the flowsheet out of a large number of alternatives and the main operating conditions

2. **Water optimization**: We design the optimal water network [3,4].

Method

Corn based ethanol

1. Energy Optimization
Structural
(Multieffect columns)
HEN

Method

Method

<table>
<thead>
<tr>
<th>Case Studies</th>
<th>Heating (MW)</th>
<th>Cooling (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>79.00</td>
<td>58.98</td>
</tr>
<tr>
<td>b</td>
<td>64.96</td>
<td>44.81</td>
</tr>
<tr>
<td>c</td>
<td>45.52</td>
<td>22.12</td>
</tr>
<tr>
<td>d</td>
<td>35.88</td>
<td>21.50</td>
</tr>
</tbody>
</table>

a- Superstructure opt.
b-Supers. + HEN
c- Supers. + HEN + Mult.
d- Supers. + HEN + Mult (opt. reflux ratio)

\[ \min Z = H \cdot \sum_{s \in SW} FW_s \cdot CFW_s + AR \cdot \sum_{t \in TU} IC_t \cdot \left( FTU^{out}_t \right)^\alpha + \frac{1}{3} \sum_{t \in TU} IC_t \cdot \left( FTU^{out}_t \right)^\alpha \]

Subject to:

- Splitter mass balances
- Mixer mass balances (bilinear)
- Process units mass balances
- Treatment units mass balances

Results

Water network

Table 1.- Inventory of units for the water networks of the bioethanol processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Process Units</th>
<th>Demand Units</th>
<th>Source Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn</td>
<td>P1: Washing</td>
<td>D1: Fermentor</td>
<td>S1: Rec Column</td>
</tr>
<tr>
<td></td>
<td>P2: Boiler</td>
<td>D2: Boiler</td>
<td>S2: Beer Column</td>
</tr>
<tr>
<td></td>
<td>P3: Cooling Tower</td>
<td>D3: Cooling tower</td>
<td></td>
</tr>
</tbody>
</table>

Treatment Units

Solids removal

Organics removal

Salt removal

Results

Switchgrass as raw material
Results

Ethanol from hydrolysis of Switchgrass

Hydrolysis and Fermentation

AFEX

Dilute acid

Rectification

Adsorption

Molecular sieves

Pervaporation

Results

Ethanol from hydrolysis of Switchgrass

Results

Ethanol from hydrolysis of Switchgrass

Results

Optimal flowsheet for the production of ethanol from hydrolysis of Switchgrass

$0.8/gal, $161MM

Results

Ethanol via gasification of Switchgrass

Decomposition of GDP in 8 subproblems

Decision levels: Gasifier

Reforming mode

Reaction of Syn Gas

Optimization of:
- Syngas composition adjustment
- Sour gases removal
- Ethanol purification removal
Results

Optimal flowsheet for the production of ethanol via gasification of Switchgrass

Major saving due to income from excess of H₂

$0.41/gal, $335MM
Results

Ethanol via gasification of Switchgrass

Water network

Results

Energy consumption: Bioethanol

Results

Water consumption: Bioethanol

Results

Hydrogen from Switchgrass

Gasification

Reforming

Partial oxidation

Steam reforming

Not only bioethanol can be produced

Results

Hydrogen from Switchgrass

Reduced order model for WGSR

\[
\text{CO}_{\text{shift\_conv}} = \frac{0.0044 \cdot T(\text{HX8, Reactor1}) + 0.0924 \cdot \text{H}_2\text{O} \to \text{CO}}{\text{H}_2\text{O} \to \text{CO} + \frac{46815}{T(\text{HX8, Reactor1})^3}};
\]

Example at 155°C

H₂O/CO ratio

- Experimental
- Predicted eq (14)

Choi et al 2003. J. Power Sources 124, 432–439

Results

Hydrogen from Switchgrass

Results

Optimal flowsheet for the production of hydrogen from Switchgrass

[Diagram showing the flowsheet with stages labeled as Pretreatment, Indirect Gasification, Steam Reforming, Scrub., HBC removal, and WGSR, with pressures and temperatures indicated.]

$0.68/\text{kg, } 148\text{MM}$

Results

FT Diesel via gasification of Switchgrass

Gasification
- Direct Gasification
- Indirect Gasification

Reforming
- Steam Reforming
- Partial Oxidation

Clean up
- Wet solids removal
- HBC removal
- WGSR
- PSA H₂

Biomass → Pretreatment → Direct Gasification → Steam Reforming → PSA CO₂ Removal → PSA H₂

Biomass → Pretreatment → Indirect Gasification → Partial Oxidation → Filter → HBC removal

Flue Gas → Catalytic → MEA → PSA CO₂ Removal → PSA H₂

Biodiesel → Distillation → Hydrocracking

Results

FT Diesel via gasification of Switchgrass

FT-Reactor

Hidrocracking

\[ \alpha = \left\{ 0.2332 \left( \frac{y_{CO}}{y_{H_2} + y_{CO}} \right) + 0.633 \right\} \times \left( 1 - 0.0039 \times \left( \frac{T_{Synthesis}}{273} + 273 \right) - 533 \right) \]

\[ w_i = \alpha^{i-1} (1-\alpha)^2 \]


Results

FT Diesel via gasification of Switchgrass

Results

Optimal flowsheet for the production of FT Diesel via gasification of Switchgrass

Results

Biodiesel production
Results

Superstructure flowsheet for the production of biodiesel

Results

Production of biodiesel from algae

Traditional recovery of algae

Extraction

New design

Results

Optimal flowsheet for the production of oil from algae


$0.17/kg
$92MM
Results

Production of biodiesel

1. Structural decisions to make. Process technologies
2. Reactor operating conditions to optimize bioDiesel production
3. Recycle of excess of methanol

Simultaneous optimization and heat integration of the process

Results

Production of biodiesel

yield = (79.444523 − 1.59614107 * T('HX24', 'Reactor5') − 3.12722176 * ratio_met − 1.14234895 * Cat − 0.01193003 * (T('HX24', 'Reactor5'))^2 + 0.75330856 * (T('HX24', 'Reactor5')) * Cat + 0.40574243 * (T('HX24', 'Reactor5')) * ratio_met + 0.175788313 * Cat^2 − 6.56010529 * Cat * ratio_met − 0.02509877 * ratio_met^2);

<table>
<thead>
<tr>
<th>Variable</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>65</td>
</tr>
<tr>
<td>Ratio methanol (mol/mol)</td>
<td>3.3</td>
<td>30</td>
</tr>
<tr>
<td>Cat (%)</td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>

Catarci & Kerpen (1999) Trans. ASAE, 42 (5), 1203-1210

Results

Production of biodiesel

$0.47/gal  $0.70/gal
$102MM    $17MM

### Summary of Results

<table>
<thead>
<tr>
<th></th>
<th>Ethanol (Hydrolysis)</th>
<th>Ethanol (Gasification &amp; Catalysis)</th>
<th>Ethanol (Gasification &amp; Fermentation)</th>
<th>FT-Diesel</th>
<th>Hydrogen (Cooking)</th>
<th>Biodiesel (Cooking)</th>
<th>Biodiesel (Algae)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total investment ($MM)</td>
<td>161</td>
<td>335</td>
<td>260</td>
<td>212</td>
<td>148</td>
<td>17</td>
<td>102</td>
</tr>
<tr>
<td>Capacity (MMgal/yr)</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60'</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>Biofuel yield (kg/kg wet)</td>
<td>0.28</td>
<td>0.20</td>
<td>0.33</td>
<td>0.24</td>
<td>0.11</td>
<td>0.96</td>
<td>0.48</td>
</tr>
<tr>
<td>Production cost ($/gal)</td>
<td>0.80</td>
<td>0.41</td>
<td>0.81</td>
<td>0.72</td>
<td>0.68'</td>
<td>0.70</td>
<td>0.47</td>
</tr>
<tr>
<td>Water consumption (gal/gal)</td>
<td>1.66</td>
<td>0.36</td>
<td>1.59</td>
<td>0.15</td>
<td></td>
<td>0.33</td>
<td>0.60</td>
</tr>
<tr>
<td>Energy consump. (MJ/gal)</td>
<td>-10.2</td>
<td>-9.5</td>
<td>27.2</td>
<td>-62.0</td>
<td>-3.84'</td>
<td>1.94</td>
<td>1.94</td>
</tr>
</tbody>
</table>

**Byproduct**

- **CO₂ Energy**
- **Energy CO₂**
- **Green Gasoline Energy CO₂**
- **Fertilizer CO₂**

Conclusions

--Biomass and waste are promising raw material for biofuels.

--The range of biofuels is broad: hydrogen, bioethanol, biodiesel, green gasoline and diesel, biomethanol....

--Mathematical programming techniques offer a powerful tool to synthesize bioprocesses to make them economically attractive and environmentally friendly.

--It is feasible to produce second generation of biofuels but further development is required in purification and reaction technologies to increase water recycle and reuse and increase the yield of the processes.
Acknowledgements

Prof. Grossmann
Dr. Ricardo Lima
Dr. Ramkumar Karuppiah
Dr. Víctor Zavala
Dr? Sebastián Terrazas
Dr? Juan Ruiz
Rosanna Franco
Rodrigo López-Negrete
Lin Lin Yang
Vijay Gupta
Ravi Karmath
Sumit Mitra
Marjtin Van Elzakker
Marcelo Escobar
Prof. Elvis Ahmetovic
Prof. Kravanja
Lidija Cucek
Mabel

Muchas gracias
University of Salamanca
from 1218

Where is the frog?
Just a hint.

For the rest, you have to visit Salamanca.