A Systematic Test of Manufacturing Property-improved Biodiesel Coupled with Butanol Extractive Fermentation

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10-7-2009
Bio-butanol, a new biofuel with high performance

**Biomass**

Sugar → Fermentation → Butanol

**Biofuel Blends**

**Worldwide Fuel Markets**

**Plant Feedstocks**

**Performance Fuels**
Fermentative Butanol production

- Traditional butanol fermentation
  - production inhibition
  - low solvents concentrations
  - large amount of energy for products recovery
- Butanol fermentation with in-situ products separation
  - extraction
  - gas stripping
  - others

A new process with 1) energy-saving; 2) waste water minimization; 3) high butanol yield via engineering method
A case of using biodiesels as butanol fermentation extractants

- Biodiesel, a green renewable energy
- Rich resources
  - originated from waste cooking oil, rap oil, palm oil, etc.
- Some disadvantages
  - combustion power low
  - cecane number low and poor ignition quality (waste cooking oil based)
- Reports: extracting butanol into biodiesels could enhance engine ignition performance & combustion power
The targets, the property-improved biodiesel manufacturing system

- Property-improved biodiesel coupled with butanol extractive fermentation
  - improving the qualities of existing biodiesel
  - direct utilization of fermentative products – energy saving
  - recycling the fermentative supernatants – waste water minimization
  - enhancement the “actual butanol yield”
  - application diversity of using biodiesels with various origins

Base extractant ➔ waste cooking oil based biodiesel
Performance of property-improved biodiesel

- With the increasing of cecane number
  - ignition delay time was shorten
  - combustion efficient was enhanced
  - black smoke emission was decreased

Taking butanol content exceeding 10 g/L of biodiesel as samples:

The cecane number of extractive butanol of biodiesel enhanced from 51.4 to 54.4

(consignation Sino Petrochemical limited company Jinling branch’s center of quality testing)
Metabolic pathway & Actual butanol yield

- Actual butanol yield:
  the ratio of butanol in biodiesel and starch consumption

- Extractive coefficient of biodiesel to butanol & constant
  1.2-1.4
  Actual butanol yield: 13%-14%

Addition tiny amount electron carrier substance to butanol fermentation

Changing carbon metabolic flow

Enhancing butanol over 30%
Decreasing acetone 50%
Butanol fermentation metabolic pathway

STARCH → GLUCOSE → PYRUVATE → ACETYL CoA → ACETO ACETYL CoA → ACETONE → BUTYRYL CoA → BUTANOL

EMP → NADH → NAD + H+ → H2 → HYDROGENASE → NADH + H+ → H2 → ELECTRON TRANSFER SYSTEM → CO2 → NAD

CARBON FLOW

ELECTRON FLOW

NAD → Fd-NAD REDUCTASE → NADH → HYDROGENASE → Fd-red → Fdox → NADH-Fd REDUCTASE → NAD → FDOX → NADH
Electron carrier to enhance “actual butanol yield”

- Adding electron carrier to force proton in excess can make the proton forced with Fd-NAD reductase over production NADH and strengthen butanol formation.
- Maybe intensify the butanol production inhibition

\[
\begin{align*}
\text{NAD} & \xrightarrow{\text{Fd-NAD REDUCTASE}} \text{NADH} \\
\text{Fd}_{\text{red}} & \xrightarrow{\text{HYDROGENASE}} \text{Fd}_{\text{ox}} \\
\text{H}^+ & \xrightarrow{\text{H}_2} \\
\text{NAD} & \xrightarrow{\text{NADH-Fd REDUCTASE}} \text{NADH}
\end{align*}
\]

Addition neural red

0.1% \((W/V)\)

Neural red & biodiesel

Conducting more high-efficiency fermentation system
Improving of butanol in biodiesel and “actual butanol yield” by adding neural red

- Compared to the control (not adding neural red)
  - Acetone concentration in the broth
  - Butanol concentration in the biodiesel
  - “Actual butanol yield”

<table>
<thead>
<tr>
<th></th>
<th>Acetone (g/L)</th>
<th>Butanol (g/L)</th>
<th>Total solvent (g/L)</th>
<th>&quot;Actual butanol yield&quot;(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oil</td>
<td>Broth</td>
<td>Oil</td>
<td>Broth</td>
</tr>
<tr>
<td>Biodiesel extraction (1:1)</td>
<td>2.87</td>
<td>7.78</td>
<td>11.29</td>
<td>8.29</td>
</tr>
<tr>
<td>Biodiesel extraction (1:1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>neural red</td>
<td>2.25</td>
<td>5.64</td>
<td>13.41</td>
<td>10.04</td>
</tr>
</tbody>
</table>
Fermentation performance & directly reusing waste supernatant

![Graph showing gas production per L-broth (L) over time (h) for different waste supernatant recycle ratios (0%, 25%, 50%, 75%).]

<table>
<thead>
<tr>
<th>Recycle ratio ( % )</th>
<th>Butanol (g/L )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oil</td>
</tr>
<tr>
<td>Traditional</td>
<td></td>
</tr>
<tr>
<td>fermentation</td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>0</td>
</tr>
<tr>
<td>25%</td>
<td>0</td>
</tr>
<tr>
<td>50%</td>
<td>0</td>
</tr>
<tr>
<td>75%</td>
<td>0</td>
</tr>
<tr>
<td>Extractive</td>
<td></td>
</tr>
<tr>
<td>fermentation</td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>9.5</td>
</tr>
<tr>
<td>25%</td>
<td>10.09</td>
</tr>
<tr>
<td>50%</td>
<td>11.15</td>
</tr>
<tr>
<td>75%</td>
<td>4.71</td>
</tr>
</tbody>
</table>

supernatant/fresh water %
Gas production of waste supernatant recycle ratio of 75% in different pretreatment mode

- Non-treatment
- Single membrane filter
- Single diatomite treatment
- Composite treatment
Solvents of waste supernatant recycle ratio of 75% in different pretreatment mode

<table>
<thead>
<tr>
<th></th>
<th>Acetone (g/L)</th>
<th>Butanol (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>6.12</td>
<td>12.24</td>
</tr>
<tr>
<td>Waste supernatant</td>
<td>1.52</td>
<td>3.31</td>
</tr>
<tr>
<td>Waste supernatant + diatomite treatment + membrane filter</td>
<td>6.01</td>
<td>11.54</td>
</tr>
<tr>
<td>Waste supernatant + diatomite treatment</td>
<td>3.21</td>
<td>6.55</td>
</tr>
<tr>
<td>Waste supernatant + membrane filter</td>
<td>3.51</td>
<td>5.71</td>
</tr>
</tbody>
</table>

Possible factors analysis?
Inhibitory factors summarization & waste supernatant recycle ratio of 75%

Inhibitory factors

- Soluble protein generating from fermentation: (×)
- Residual solvents: (×)
- Soluble large molecular pigment: (√)
- Other unknown inhibitory small molecular: (√)
- Residual sugars: (×)

The key of waste supernatant stable recycle ratio of 75% to remove the residual butanol before pretreatment

- Acetone: (×)
- Butanol: (×)
- Residual butanal after sterilization: (×)
- Produced in the process of gelatinization and sterilization: (?)
Available biodiesels diversity and stability

- Various biodiesel: waste cooking oil, rap oil, soybean oil and palm oil
- Fermentation performance of biodiesel based waste cooking oil under the condition of different seasons

![Graph showing fermentation performance in winter and spring vs. summer]

- Winter and spring
- Summer

Legend:
- Traditional fermentation
- Extractive fermentation
Fermentation performance of soybean biodiesel

- **Extractant**: soybean biodiesel
- **Composite treatment**: diatomite treatment and membrane filter
- **Residual butanol & non-in-situ removal from waste supernatant & to ensure the more stability of fermentation performance**
- **Residual butanol by oleyl alcohol extraction & enhancing actual butanol yield**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Acetone (g/L)</th>
<th>Butanol (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>6.86</td>
<td>13.22</td>
</tr>
<tr>
<td>Supernatant</td>
<td>1.43</td>
<td>3.87</td>
</tr>
<tr>
<td>Supernatant + removal butanol</td>
<td>2.05</td>
<td>4.14</td>
</tr>
<tr>
<td>Supernatant + removal butanol + composite treatment</td>
<td>6.69</td>
<td>12.81</td>
</tr>
<tr>
<td>Supernatant + composite treatment</td>
<td>4.35</td>
<td>8.15</td>
</tr>
</tbody>
</table>

[Graph showing gas production per L-broth over time with different treatment conditions.]

[Table showing acetone and butanol levels in different treatments.]

[Arrow pointing to removal butanol from supernatant.]

[Arrow pointing to oleyl alcohol.]

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**Diagram:**

- Chart showing gas production per L-broth over time with different treatment conditions.
- Table showing acetone and butanol levels in different treatments.

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**Notes:**

- Extractant: soybean biodiesel
- Composite treatment: diatomite treatment and membrane filter
- Residual butanol & non-in-situ removal from waste supernatant & to ensure the more stability of fermentation performance
- Residual butanol by oleyl alcohol extraction & enhancing actual butanol yield
Enhancing the whole “actual butanol yield” & waste supernatant stability recycle

- **Butanol**
- **Supernatant tank**
- **Fermentor**
  - **Broth**
  - **Extractant**
  - **Diatomite treatment** & **Membrane filter**
  - **Recycle ratio of 75%**
- **Initial biodiesel tank**
- **Property-improved biodiesel tank**

**Diagram Notes:**
- Fresh water
- Corn flour
- **Non-in-situ extraction butanol**
Acknowledgement

We thank the kind support from the natural fund #20976072 from China state government

Thanks for your attention