Green Production of Biodiesel and Biofuels With Solid- & Nano-catalysts

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Conversion of Lignocelluloses and Oil

1. Thermal Conversions
   Pyrolysis, Gasification, Combustion), $T > 300 \, ^\circ C$

2. Bio conversion
   Microbial Lipids, Pretreatment for Hydrolysis, Biogas, Biohydrogen, Butanol) $T < 50 \, ^\circ C$

3. Catalytical Chemical Conversions
   Biodiesel, DMF (2,5-Dimethylfuran), ML (Methyl Levulinate), GVL ($\gamma$-Valerolactone)
1. Biodiesel

Methyl esters (biodiesel)

\[
\begin{align*}
\text{CH}_2\text{COOR}_1 & \quad \text{CH}_2\text{OH} \\
\mid & \quad \text{Catalyst} \\
\text{CH}_2\text{COOR}_2 + 3\text{CH}_3\text{OH} & \rightarrow \text{CHOH} + R_1\text{CO}_2\text{CH}_3 + R_2\text{CO}_2\text{CH}_3 + R_3\text{CO}_2\text{CH}_3 \\
\mid & \quad > 60 \, ^\circ\text{C} \\
\text{CH}_2\text{COOR}_3 & \quad \text{CH}_2\text{OH}
\end{align*}
\]

Tryglyceride \((R_1-R_3 = C_{13}-C_{18})\)

Two problems:

- Raw Materials (Jatropha oil and Microbial lipids)
- Catalyst (\(\text{NaOH}\)) – Solid Catalysts

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1.1 Microbial Lipids from Straw

Crop straws

Lignocellulose

Undissolved solid

Cellulose

Enzyme hydrolysis

Lipid fermentation

Oleaginous yeast

Extraction

Lignin

Acid-soluble lignin

Xylose, Arabinose, ...

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New cultivar of *Jatropha* bred in Xishuangbanna Tropical Botanical Garden (a: old cultivar, b: new cultivar): (A) seedlings (B) adult trees, (C) fruiting, (D) ripening fruits.

1.2 Ultrasonic Production of *Jatropha* Biodiesel

**Two-step:** 2 h $\rightarrow$ 0.5 h [Fatty acid methyl esters (FAMEs)]

*Jatropha* oil: high acid value e.g., 5-15 KOH/g

With NaOH

- Saponification
- Difficult separation

**Saponification:**

\[
\begin{align*}
\text{CH}_2\text{OOCR}_1 + \text{CHOOCR}_2 + \cdot 3\text{H}_2\text{O} & \rightarrow \text{CH}_2\text{OH} + \text{R}_1\text{COOH} \\
\text{CH}_2\text{OOCR}_3 + \cdot 3\text{H}_2\text{O} & \rightarrow \text{CH}_2\text{OH} + \text{R}_2\text{COOH}
\end{align*}
\]

\[
\begin{align*}
\text{RCOOH} + \text{NaOH} & \rightarrow \text{RCOONa} + \cdot \text{H}_2\text{O}
\end{align*}
\]

Step 1: esterification-$\text{H}_2\text{SO}_4$; Step 2: trans-esterification-$\text{NaOH}$

Microwave Production with Sodium Silicate

Calcined Sodium Silicate:

Rapeseed Biodiesel

2 h → 5 min
Biodiesel yield > 93%

Saponification

crude Jatropha oil

Jatropha Biodiesel

Pretreated crude Jatropha oil


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Ultrasonic Production of Biodiesel with Basic Calcined Hydrotalcite Nanoparticles

Calcined Hydrotalcite:

- Biodiesel
- Glycerol

Magnetic (Na$_2$SiO$_3$@Fe$_3$O$_4$/C) catalyst was used for biodiesel production (90.7% yield) directly from Jatropha oil with high acid value (4.8 mg KOH/g) by ultrasonic (0.1 W/mL) and magnetic stirring (200 rpm). The catalyst was easily magnetically separated for recycles.

One-Step Biodiesel Production from High-acid Value *Jatropha* Oil in Ionic Liquids

**Why Ionic Liquids (ILs)?**
- Easy separation
- Recyclable
- Good solvents
- *Lewis* and *Franklin* acid

- F. Guo, Z. Fang*, Chinese invention patent #: CN 201110080223.X.

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Production of Biodiesel from Sulfonated Lignin Char

Raw kraft lignin

Kraft lignin char without chemical activation

Kraft lignin char after chemical activation by $\text{H}_3\text{PO}_4$

Sulfonated kraft lignin char (catalyst)

96% biodiesel yield

*Jatropha oil with high-acid value (12.7 mg KOH/g)


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A novel magnetic carbonaceous acid catalyst was synthesized from glucose and iron chloride by a new method of double hydrothermal precipitation and pyrolysis, and subsequent sulfonation. The catalyst presents high active, stable and recoverable in the production of *Jatropha* biodiesel with high yields for 3 cycles (90.5%, 91.8%, 90.3%), slight reduction in total acid density (2.43 vs. 2.79 mmol/g) and high catalyst recovery rate of 96.3%.

Waste lignin

Carbonization: 180 °C, 7.8 MPa
Subcritical ethanol

Carbonization: 260 °C, 8.4 MPa
Supercritical ethanol

Pyrolysis: 400 °C

Biochars

Sulfonation

Catalyst with high acid content

Biodiesel (> 90%) from crude Jatropha oil

M Huang, J Luo, Zhen Fang*, H Li, Applied Catalysis B: Environmental, 190, 103–114 (2016).

Graphical abstract: Lignin was carbonized in ethanol and sulfonated to carbonaceous solid acids with high acid content (> 5 mmol [H⁺]/g) for biodiesel production. High biodiesel yield (> 95%) was achieved from oleic acid with 5 cycles. Biodiesel yields (> 90%) were obtained from Jatropha and blended soybean oils with high acid values.
Production of biodiesel from plant oil catalyzed by magnetic Na$_2$SiO$_3$@Ni/C and H$_2$ from by-product crude glycerol with deactivated Na$_2$SiO$_3$@Ni/C.

Graphical abstract

Jatropha seeds were extracted oil for biodiesel production and the hulls were carbonized to load active sites as magnetic carbonaceous solid acid and base catalysts. Crude Jatropha oil was esterified to decrease its acid value to 1.3 from 17.2 mg KOH/g by the solid acid, and subsequently transesterified to biodiesel (96.7% yield) catalyzed by the solid base. After 3 cycles and magnetically separated, the deactivated base was catalyzed the hydrothermal gasification of biodiesel by-product (crude glycerol) with gasification rate of 81% and 82% H₂ purity.


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Biodiesel yield: \( \geq 87 \text{ wt}\% \) at 90 \(^\circ\)C for 2 h with 10 cycles

Total acid content: \( 8.45 \text{ mmol/g} \)

Carbonaceous acid catalyst with high acid content (Lewis and Bronsted acid) was synthesized by metal (Zr) ion chelation and sulfonation of sodium carboxymethylcellulose. With the catalyst for esterification of oleic acid, biodiesel yield could reach \( > 99\% \) at 40-90 \(^\circ\)C, with 3-4 catalyst cycles.

**Graphical abstract:**

Carbonaceous **bifunctional magnetic solid acid catalyst** with high acid content was synthesized by four-step method: (i) metal (Fe) ion chelation, (ii) calcination, (iii) metal (Zr) ion chelation and embedding, and (iv) sulfonation. It efficiently catalyzed the esterification of oleic acid, transesterification of soybean oil and pretreatment of *Jatropha* oil with easy separation for 10 cycles and high stability.

<table>
<thead>
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<th>Application</th>
<th>8.84 mmol/g applications</th>
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<tr>
<td>Esterification of free fatty acids</td>
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<tr>
<td>Transesterification of oils</td>
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**Esterification of free fatty acids**

**Transesterification of oils**

**Pretreatment of *Jatropha* oil**

**Magnetically separated for cycles**
Activated Mg-Al hydrotalcite nanoparticles (< 45 nm) were synthesized. The catalyst presented both acidic and basic to produce biodiesel from oils with high acid value (AV). Biodiesel yield reached 93.4% and 92.9% from *Jatropha* and soybean oils with AV of 6.3 and 12.1 mg KOH/g. The catalyst can recycle 4 times with *Jatropha* biodiesel yield > 86%.

Graphical abstract:
Alkaline oxides concerted with acidic -COOFe structure, for the one-pot esterification and transesterification of high AV Jatropha oils without saponification. Zn$_8$@Fe-C$_{400}$ achieved nearly 100% Jatropha biodiesel yield at 160 °C within 4 h, and was used for at least 10 cycles with biodiesel yield of >94.3% at AV of 6.3 mg KOH/g.

F Zhang, Zhen Fang*, et al., A Continuous Flow Reactor for the Production of Soluble Sugars and Biodiesel. Chinese patent (utility model): ZL201420785283.0 (June 2015). (GRANTED)
Pilot *Jatropha* Biodiesel Plant

2. Reaction routes for the valorization of biomass with catalytic methods

(L = Lewis, B = Bronsted, [H] = Hydrogenation, [O] = Oxidation, [HDO] = Hydrideoxygenation, HMF = 5-hydroxymethylfurfural, EMF = 5-ethoxymethylfurfural, DMF = dimethylfuran, DMTHF = 2,5-dimethyltetrahydrofuran, FDCA = 2,5-furandicarboxylic acid, FfA = furfuryl alcohol, MF = 2-methylfuran, MTHF = 2-methyltetrahydrofurfural, MA = maleic anhydride, THF = tetrahydrofuran, LA = levulinic acid, GVL = γ-valerolactone)

One-pot and efficient production of furanic/aromatic hydrocarbons (>95% yields) from biomass derivatives is achieved under mild conditions (25-130 °C) by using readily available polymethylhydrosiloxane (PMHS) as liquid H-donor over hydrophonic Pd nanoparticles on MOFs.

A novel biomass-derived mesoporous bifunctional hybrid (FDCA-Hf) prepared by facile assembly of 2,5-furandicarboxylic acid (FDCA) with hafnium (Hf) was highly stable and active for the production of biofuels and valuable chemicals from bio-based compounds such as ketones, aldehydes and acidic oils via acid-base cooperative catalysis.

H Li, TT Yang, Z Fang*, *Applied Catalysis B: Environmental, 227, 79 (2018).
Interdisciplinary Combination

Nanotechnology (catalysis)
Green chemistry (ionic liquids, SCFs)
Microbial tech
Chem./Bio process

Lignocelluloses wastes

Bio-refinery

Biofuels (gas, liquid), chemicals, materials, food, pharmaceuticals

Microwave ultrasound

Integration the 4 areas (nano, green chem., microbial and eng.) to effectively refine biomass wastes

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