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

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Oct. 23 ， 2018

Conversion of Lignocelluloses and Oil

1. Thermal Conversions

Pyrolysis, Gasification, Combustion), T > 300 °C

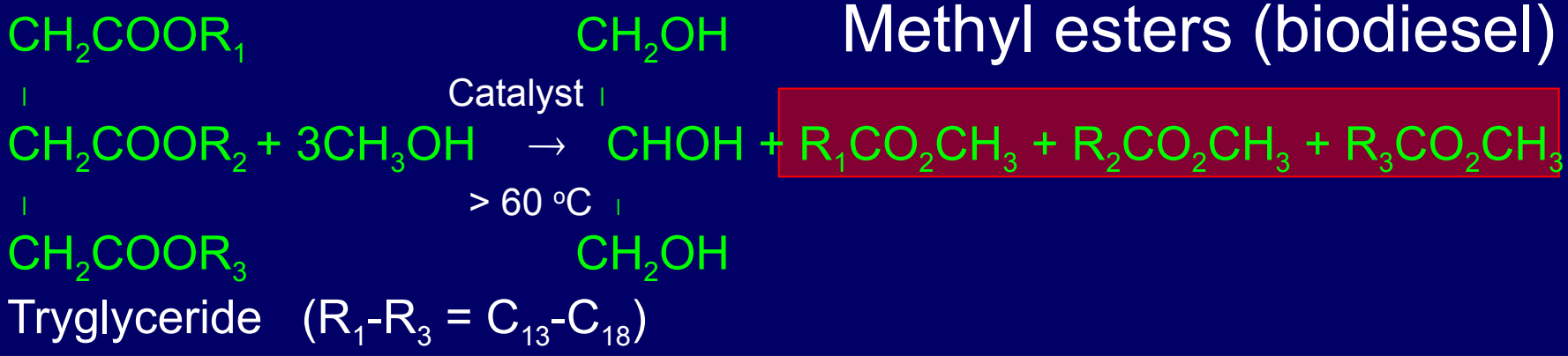
2. Bio conversion

Microbial Lipids, Pretreatment for Hydrolysis, Biogas, Biohydrogen, Butanol) T < 50 °C

3. Catalytical Chemical Conversions

Biodiesel, DMF (2,5-Dimethylfuran), ML (Methyl Levulinate), GVL (γ-Valerolactone)

1. Biodiesel

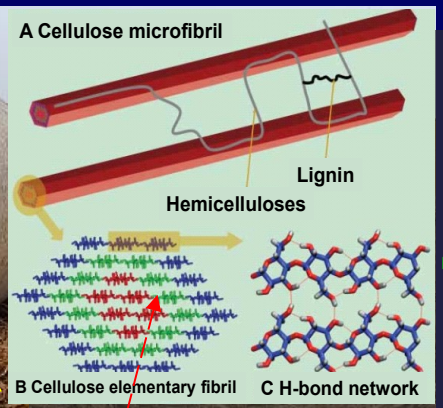


Two problems:

- **Raw Materials (Jatropha oil and Microbial lipids)**
- **Catalyst (NaOH) –Solid Catalysts**

1.1 Microbial Lipids from Straw

Crop straws



1

Ball mill extrusion

+

Solvent treatment (HPHT)

Coupled pretreatment

Acid-soluble lignin

Xylose,

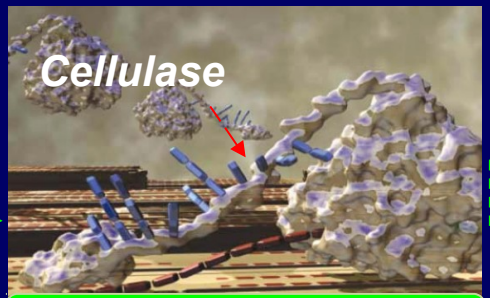
Arabinose,

...

Lignocellulose

Undissolved solid

2



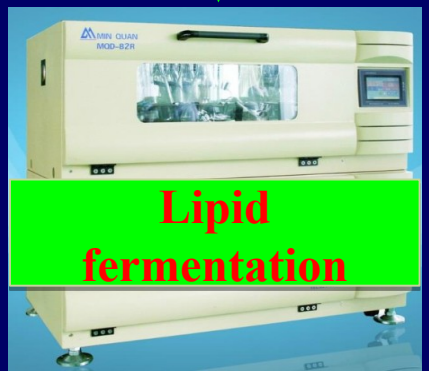
Enzyme hydrolysis

Extraction

Lignin

Oleaginous yeast

3



Lipid fermentation

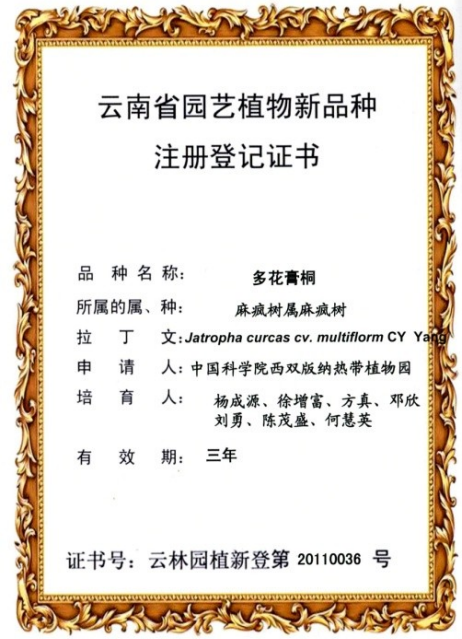
Extraction

Microbial lipids

Biodiesel: Two New *Jatropha* Varieties Bred

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

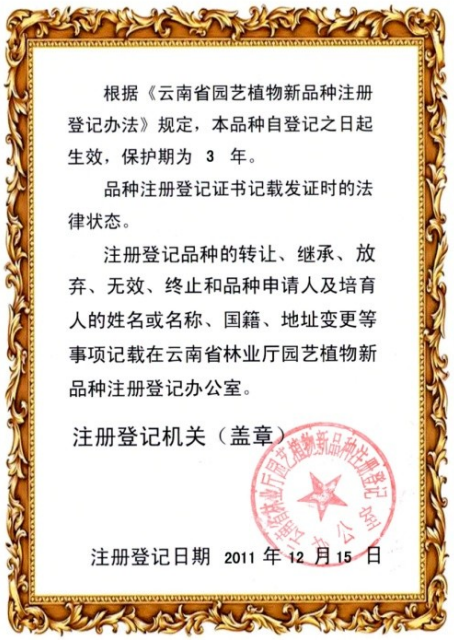
Certificates from Yunnan Government



云南省园艺植物新品种
注册登记证书

品 种 名 称： 多花膏桐
所属的属、种： 麻疯树属麻疯树
拉 丁 文：*Jatropha curcas cv. multiflorm* CY Yang
申 请 人：中国科学院西双版纳热带植物园
培 育 人： 杨成源、徐增富、方真、邓欣刘勇、陈茂盛、何慧英
有 效 期： 三年

证书号：云林园植新登第 20110036 号



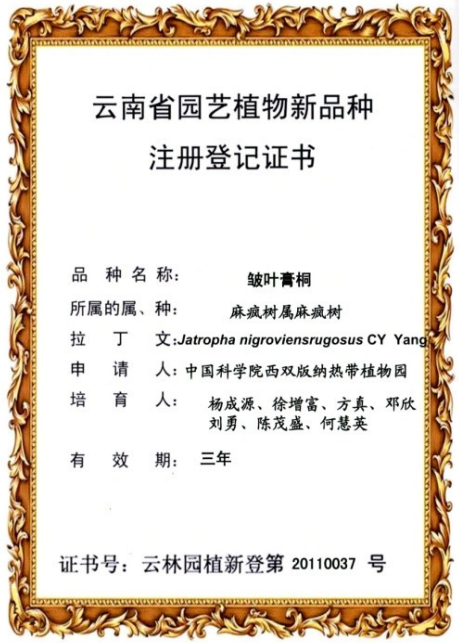
根据《云南省园艺植物新品种注册登记办法》规定，本品种自登记之日起生效，保护期为 3 年。

品种注册登记证书记载发证时的法律状态。

注册登记品种的转让、继承、放弃、无效、终止和品种申请人及培育人的姓名或名称、国籍、地址变更等事项记载在云南省林业厅园艺植物新品种注册登记办公室。

注册登记机关（盖章）

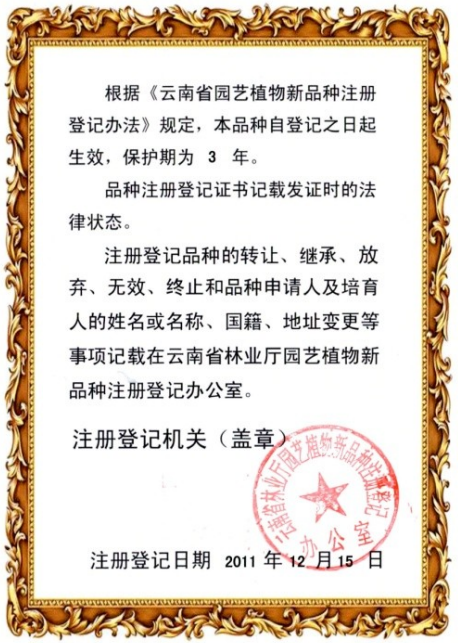
注册登记日期 2011 年 12 月 15 日



云南省园艺植物新品种
注册登记证书

品 种 名 称： 皱叶膏桐
所属的属、种： 麻疯树属麻疯树
拉 丁 文：*Jatropha nigroviensrugosus* CY Yang
申 请 人：中国科学院西双版纳热带植物园
培 育 人： 杨成源、徐增富、方真、邓欣刘勇、陈茂盛、何慧英
有 效 期： 三年

证书号：云林园植新登第 20110037 号



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注册登记品种的转让、继承、放弃、无效、终止和品种申请人及培育人的姓名或名称、国籍、地址变更等事项记载在云南省林业厅园艺植物新品种注册登记办公室。

注册登记机关（盖章）

注册登记日期 2011 年 12 月 15 日

- C.Y. Yang, Z.F. Xu, **Z Fang** et al, *Jatropha* nigroviensrugosus CY Yang, Certificate#: Yunlin Yuanzhi Xindeng 20110037, The Forestry Department of Yannan province, Dec. 15, 2011.
- C.Y. Yang, Z.F. Xu, **Z Fang** et al, *Jatropha* curcas cv. multiflorm CY Yang, Certificate#: Yunlin Yuanzhi Xindeng 20110036, The Forestry Department of Yannan province, Dec. 15, 2011.

1.2 Ultrasonic Production of *Jatropha* Biodiesel

Two-step: 2 h → 0.5 h [Fatty acid methyl esters (FAMEs)]

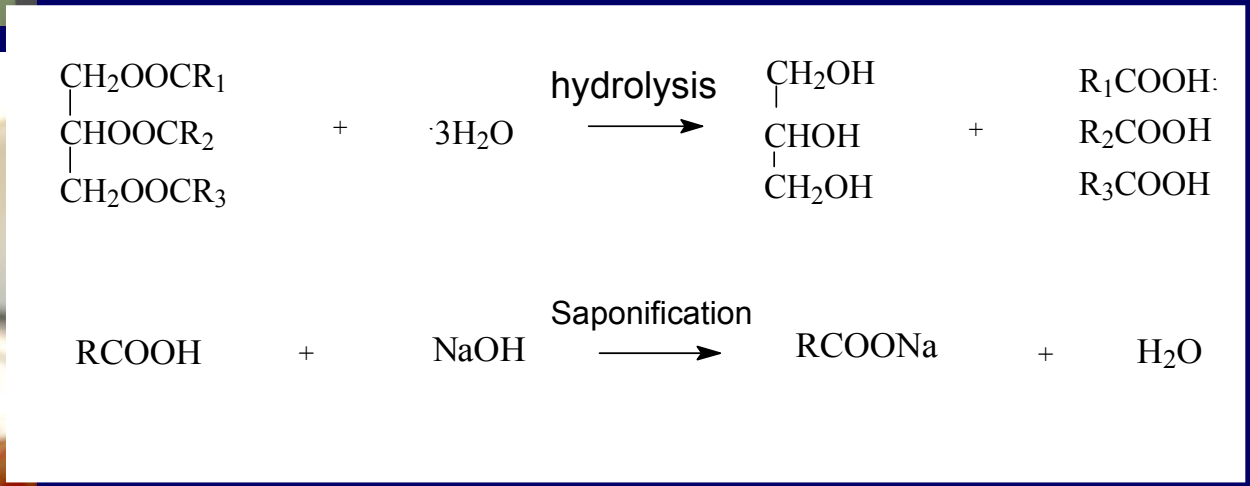
***Jatropha* oil: high acid value e.g., 5-15 KOH/g**

With NaOH

- Saponification
- Difficult separation

X Deng, Z Fang* et al., *Energy Conversion and Management*, 51, 2802-2807 (2010)

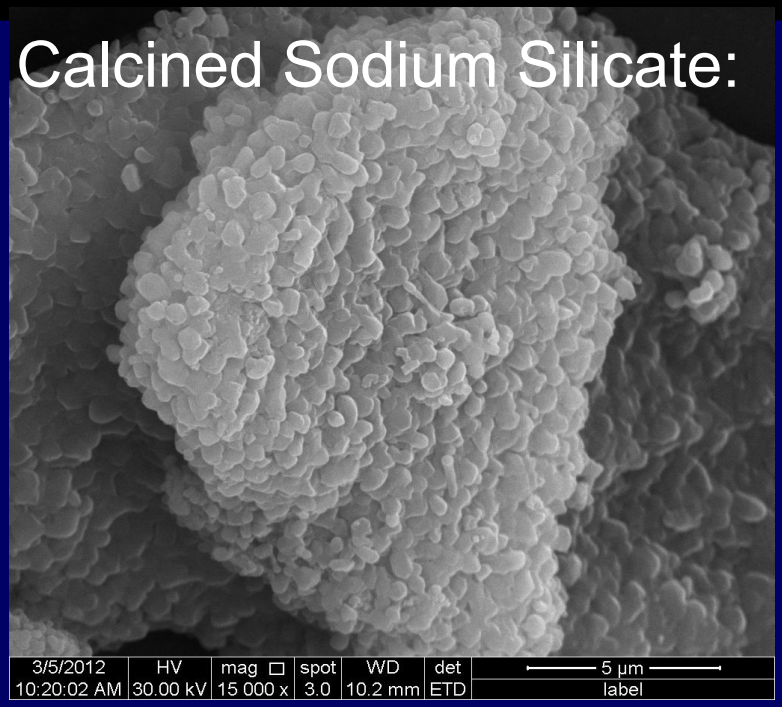
Saponification:



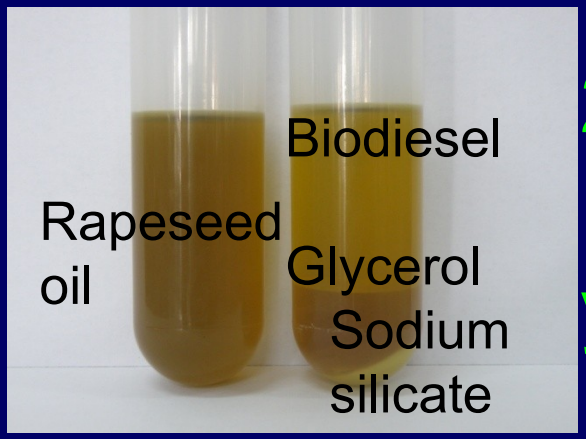
Step 1: esterification-H_2SO_4; Step 2: trans-esterification-NaOH

Microwave Production with Sodium Silicate

Calcined Sodium Silicate:

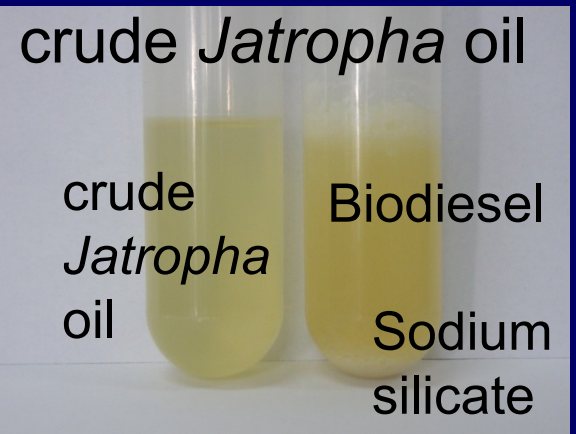


Rapeseed Biodiesel

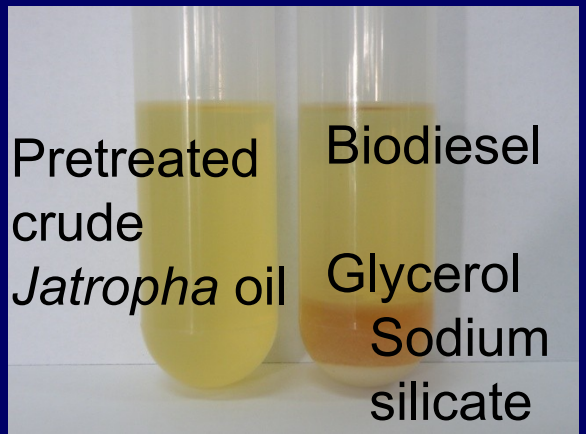


2 h → 5 min
Biodiesel yield > 93%

Saponification crude *Jatropha* oil



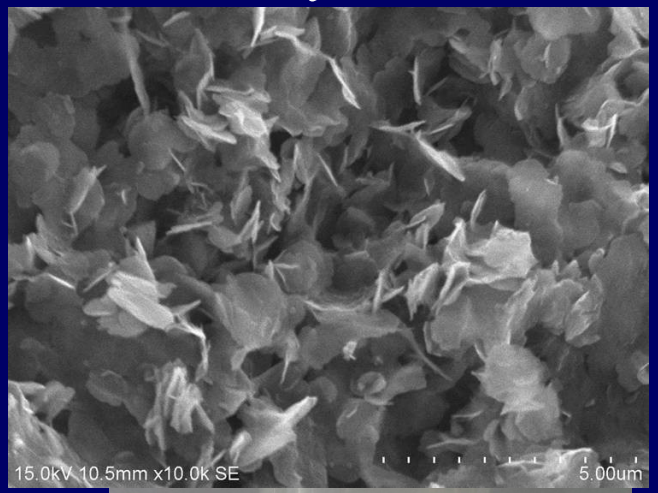
Jatropha Biodiesel

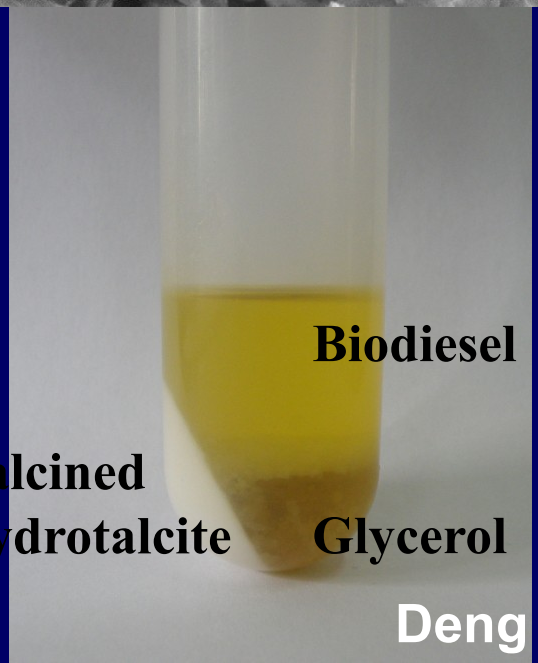


YD Long, Z Fang* et al., *Applied Energy*, 113, 1819-1825 (2014).

Ultrasonic Production of Biodiesel with Basic Calcined Hydrotalcite Nanoparticles

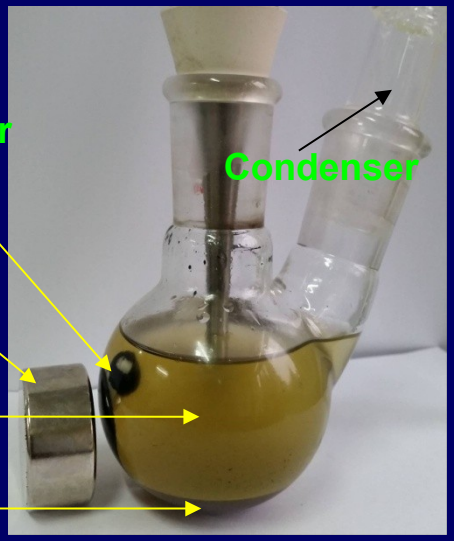
- Calcined Hydrotalcite:



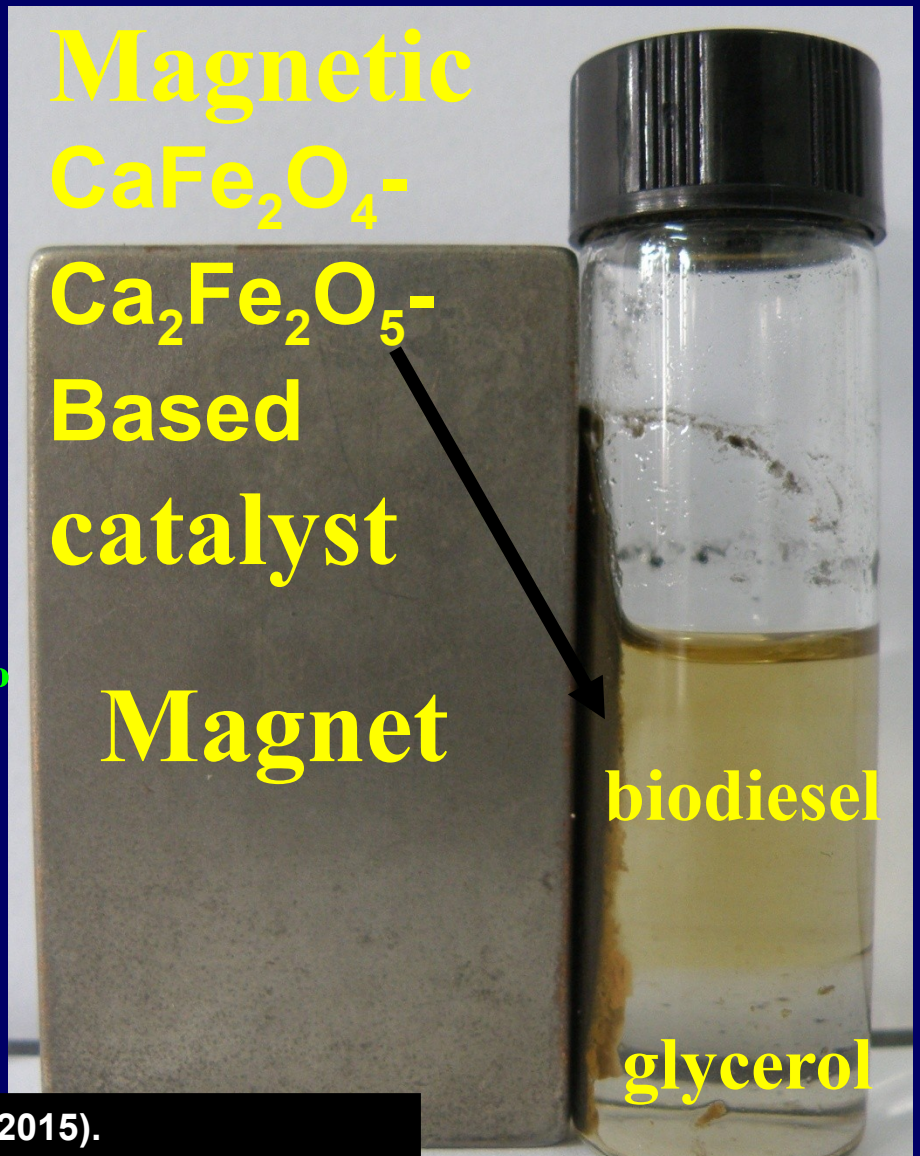


Deng X, Fang Z* et al, *Energy*, 36, 777-784 (2011)

Biodiesel Production with Magnetic Catalyst

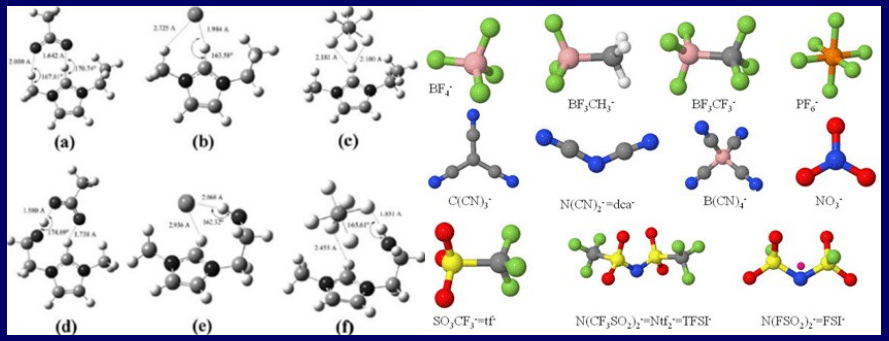


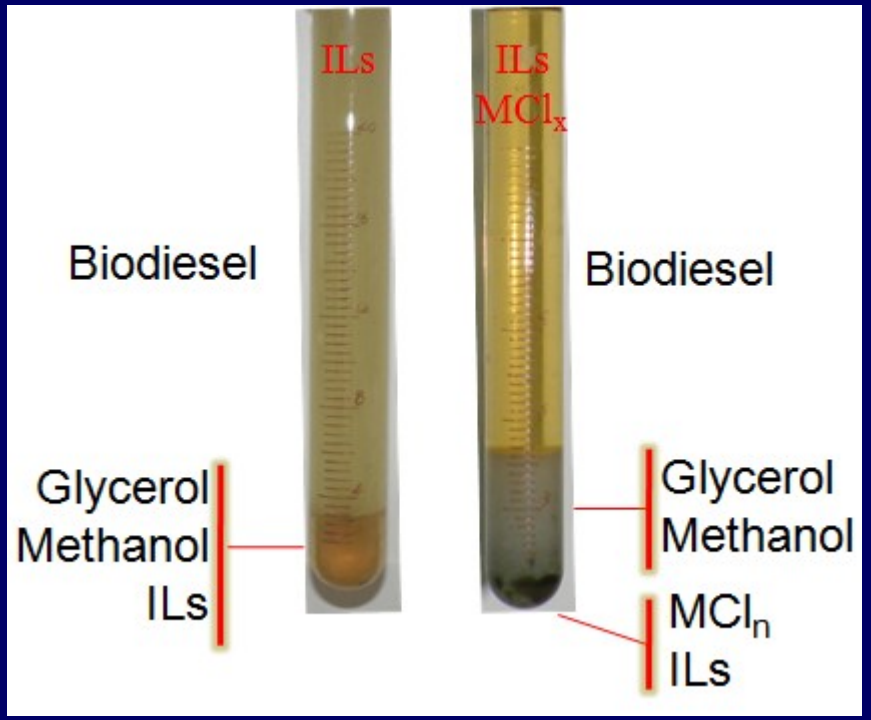
Magnetic ($Na_2SiO_3@Fe_3O_4/C$) catalyst was used for biodiesel production (90.7% yield) directly from Jatropha oil with high acid value (4.8 mg KOH/g) by ultrasonic (0.1 W/mL) and magnetic stirring (200 rpm). The catalyst was easily magnetically separated for recycles.



F. Zhang, Zhen Fang*, Y.T. Wang, *Fuel*, 150, 370–377 (2015).
Xue BJ, Fang Z* et al, *Energy*, 68, 584-591 (2014). Patent: ZL201220038727.5

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



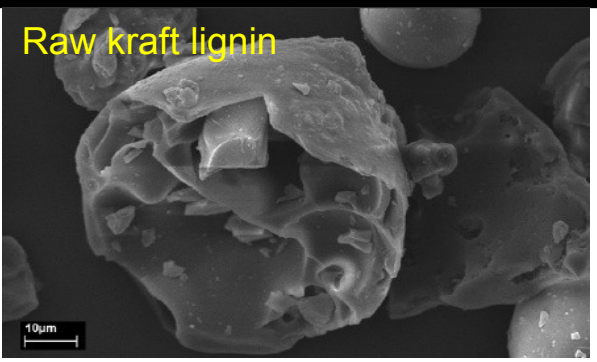


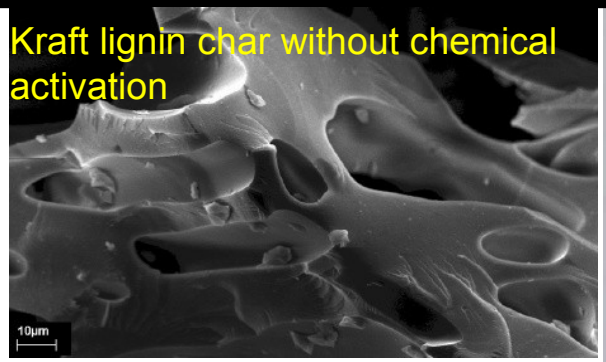
Why Ionic Liquids (ILs)?

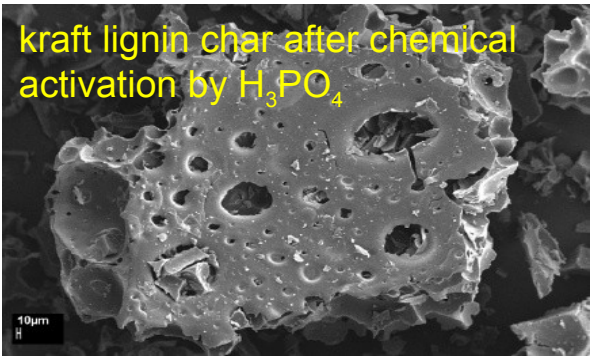
- **Easy separation**
- **Recyclable**
- **Good solvents**
- ***Lewis* and *Franklin* acid**

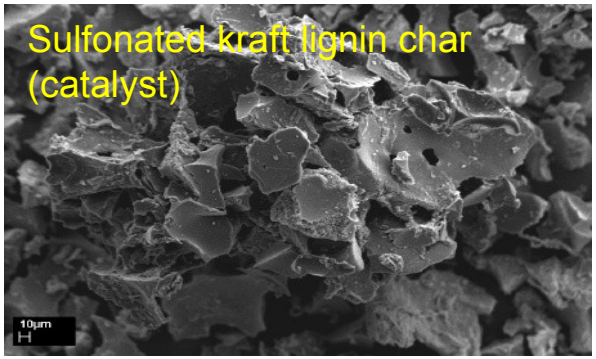
- F. Guo, **Z. Fang*** et al., *Bioresource Technology*, 2011, 102 (11): 6469-6472.
- F. Guo, **Z. Fang***, Chinese invention patent #: CN 201110080223.X.

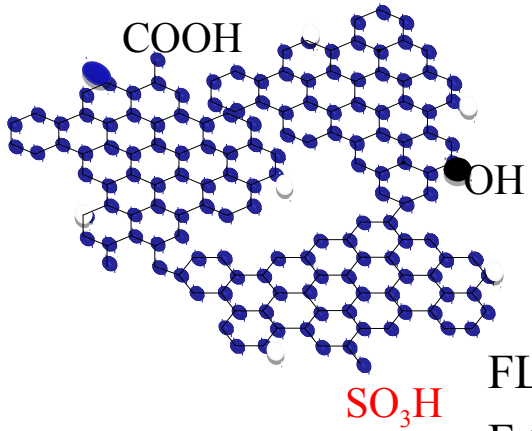
Production of Biodiesel from Sulfonated Lignin Char



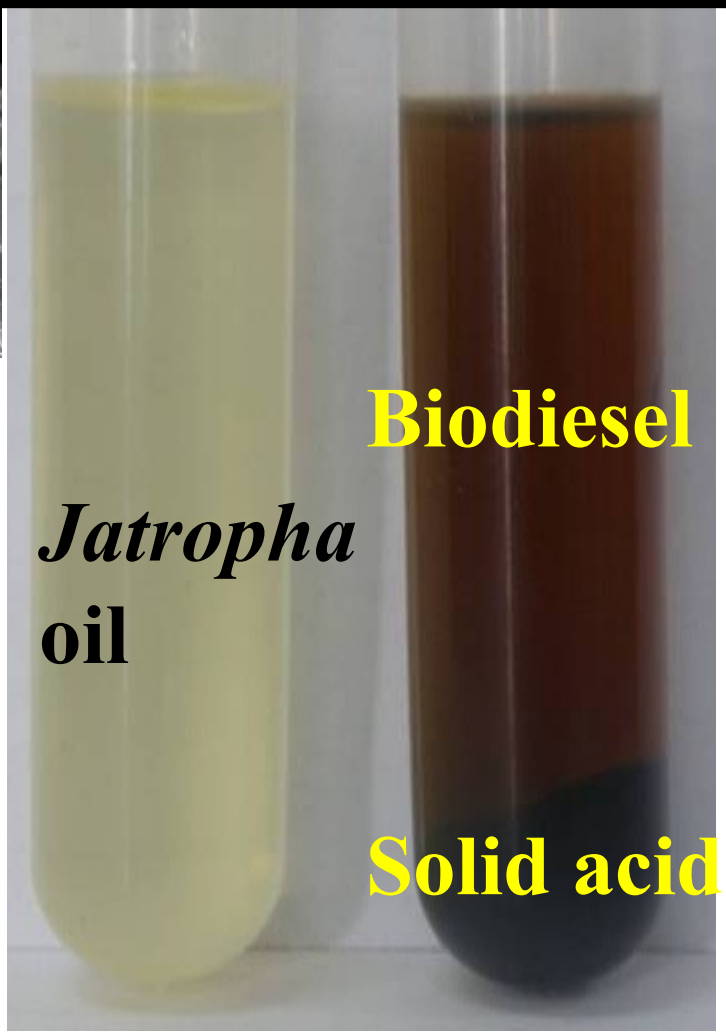






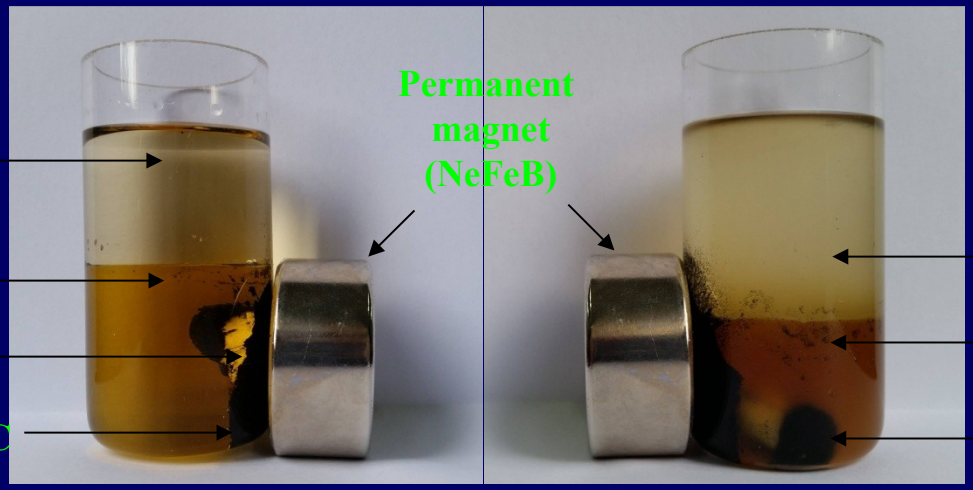


96% biodiesel yield
Jatropha oil with high-acid value (12.7 mg KOH/g)



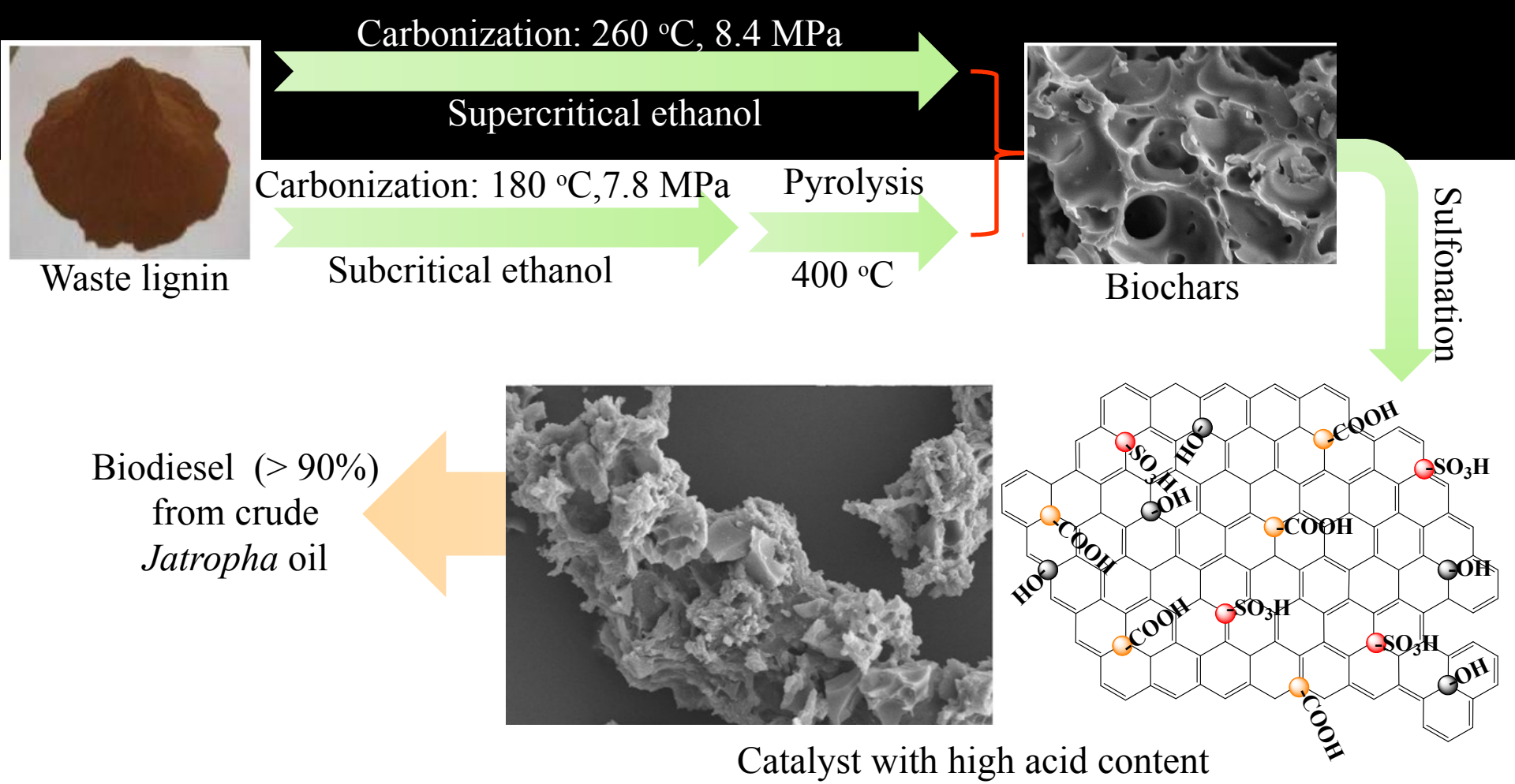
FL Pua, **Z Fang***, et al.. ***Biotechnology for Biofuels***, 2011, 4:56.
F Guo, **Z Fang***, et al. Patent: *ZL201110080225.9*

Production of Biodiesel from Magnetic Sulfonated Acid



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%.

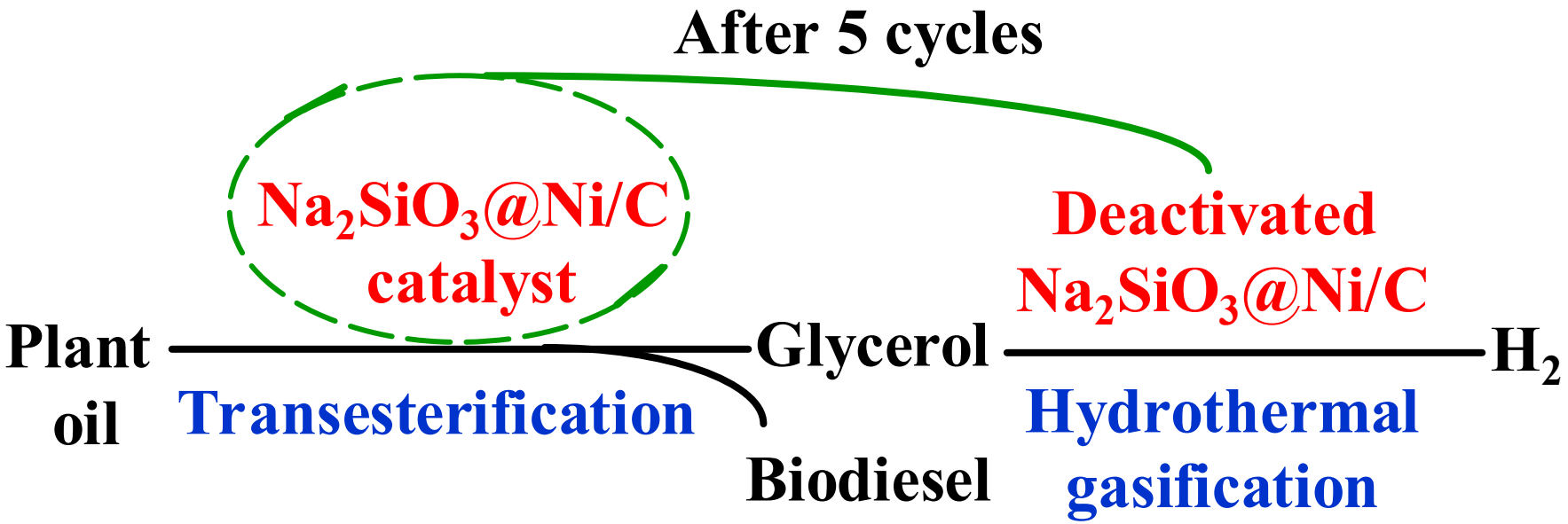
F Zhang, **Z. Fang*** et al., *Applied Energy,* 155, 637–647 (2015)



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

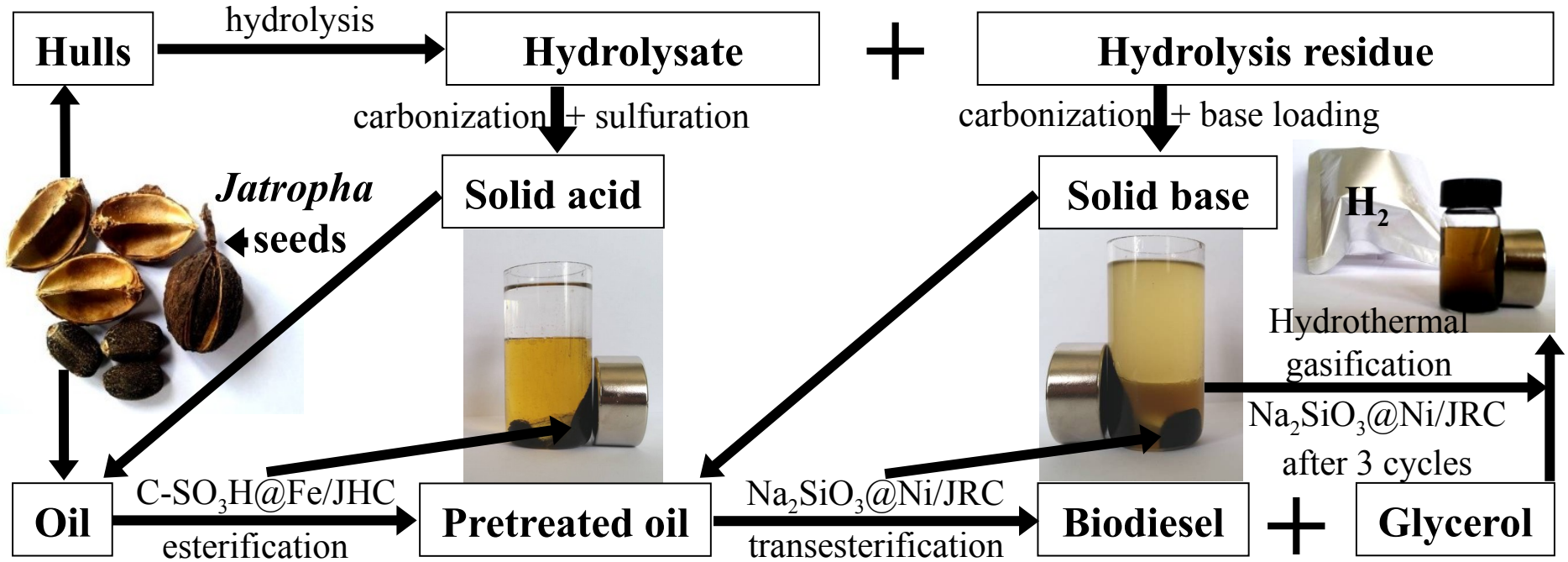
Graphical abstract： Lignin was carbonized in ethanol and sulfonated to carbonaceous solid acids with high acid content (> 5 mmol [H^+]/g) for biodiesel production. High biodiesel yield (> 95%) was achieved from oleic acid with 5 cycles. Biodiesel yields (> 90%) were obtained from *Jatropha* and blended soybean oils with high acid values.

Production of Biodiesel and Hydrogen from Plant Oil



Production of biodiesel from plant oil catalyzed by magnetic Na_2SiO_3@Ni/C and H_2 from by-product crude glycerol with deactivated Na_2SiO_3@Ni/C.

F Zhang, XH Wu, M Yao, **Zhen Fang***, YT Wang, Green Chemistry, 18, 3302-3314 (2016).



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% H_2 purity.

F Zhang, XF Tian, **Zhen Fang***, et al., Energy Conversion and Management, 142, 107–116 (2017).

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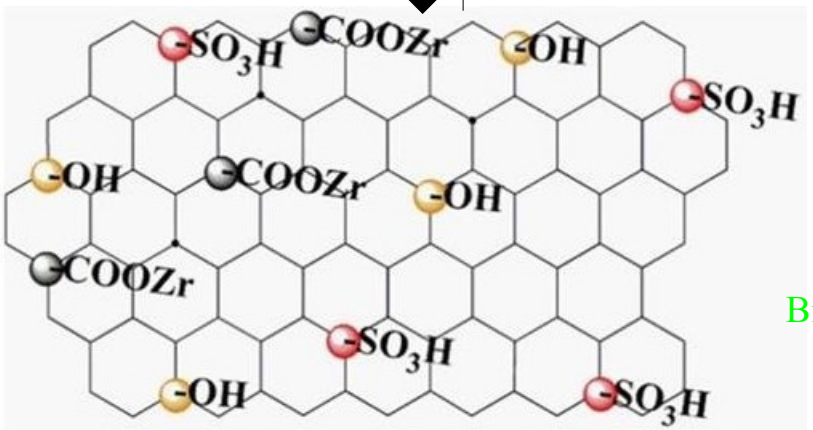
Esterification of oleic acid to biodiesel catalyzed by a highly acidic carbonaceous catalyst

CMC

sodium carboxymethyl cellulose + $ZrOCl_2 \cdot 8H_2O$

Chelation at room temperature (20-25 °C)

Sulfonation at 150 °C for 16 h



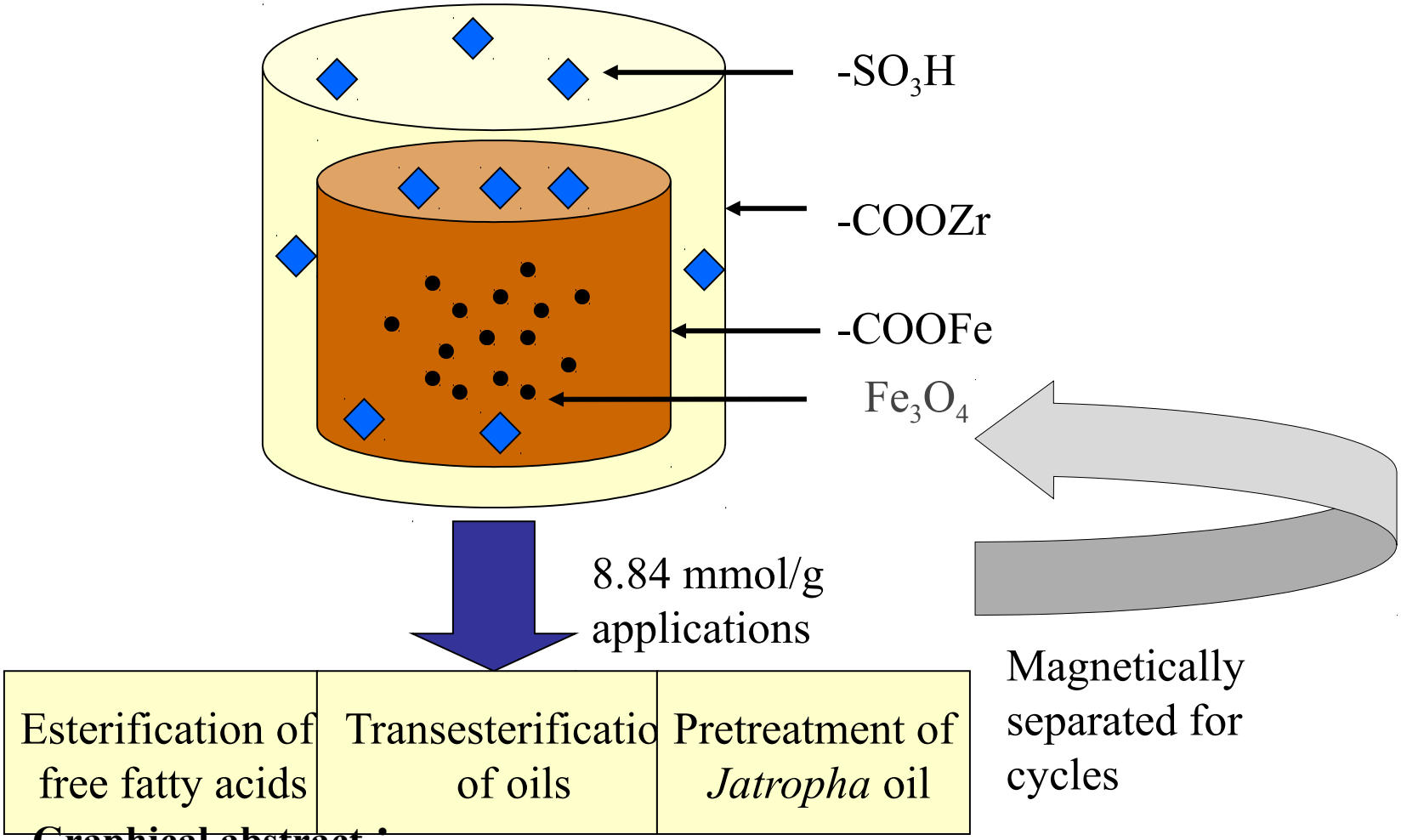
Biodiesel production

Biodiesel yield: ≥ 87 wt% at 90 °C for 2 h with 10 cycles

Total acid content: 8.45 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 °C, with 3-4 catalyst cycles.

YT Wang, **Z. Fang*** et al., *Catalyst Today*, https://doi.org/10.1016/j.cattod.2018.06.041(2018)

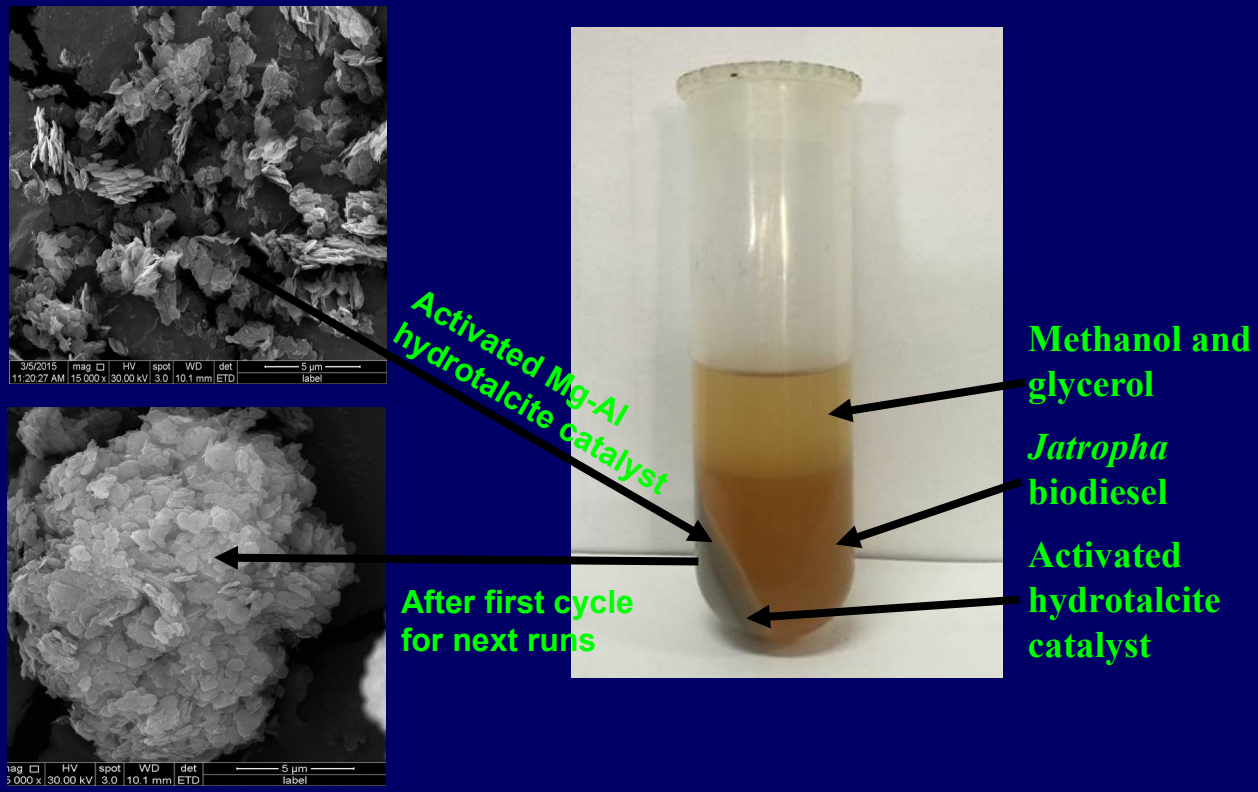


Graphical abstract：

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.

YT Wang, **Z. Fang*** et al., *Applied Energy,* **204**, 702–714(**2017**).

One-Step Biodiesel Production from High-acid Value Oils with Activated Mg-Al hydrotalcite nanoparticles



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%.

YT Wang, **Z. Fang*** et al., *Bioresource Technology*, 193, 84-89 (2015).

1、 Chelation and embedded
2、 Calcination

Magnetic acid-base amphoteric catalysts

($ZnFe_2O_4$, ferrihydrite, zincite, maghemite and magnetite)

Magnetic separation ($ZnFe_2O_4$, maghemite and magnetite)

Biodiesel

Triglycerides and free fatty acids

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 .

YT Wang, **Z. Fang*** et al., *Chemical Engineering Journal,* 348, 929-939 (2018).

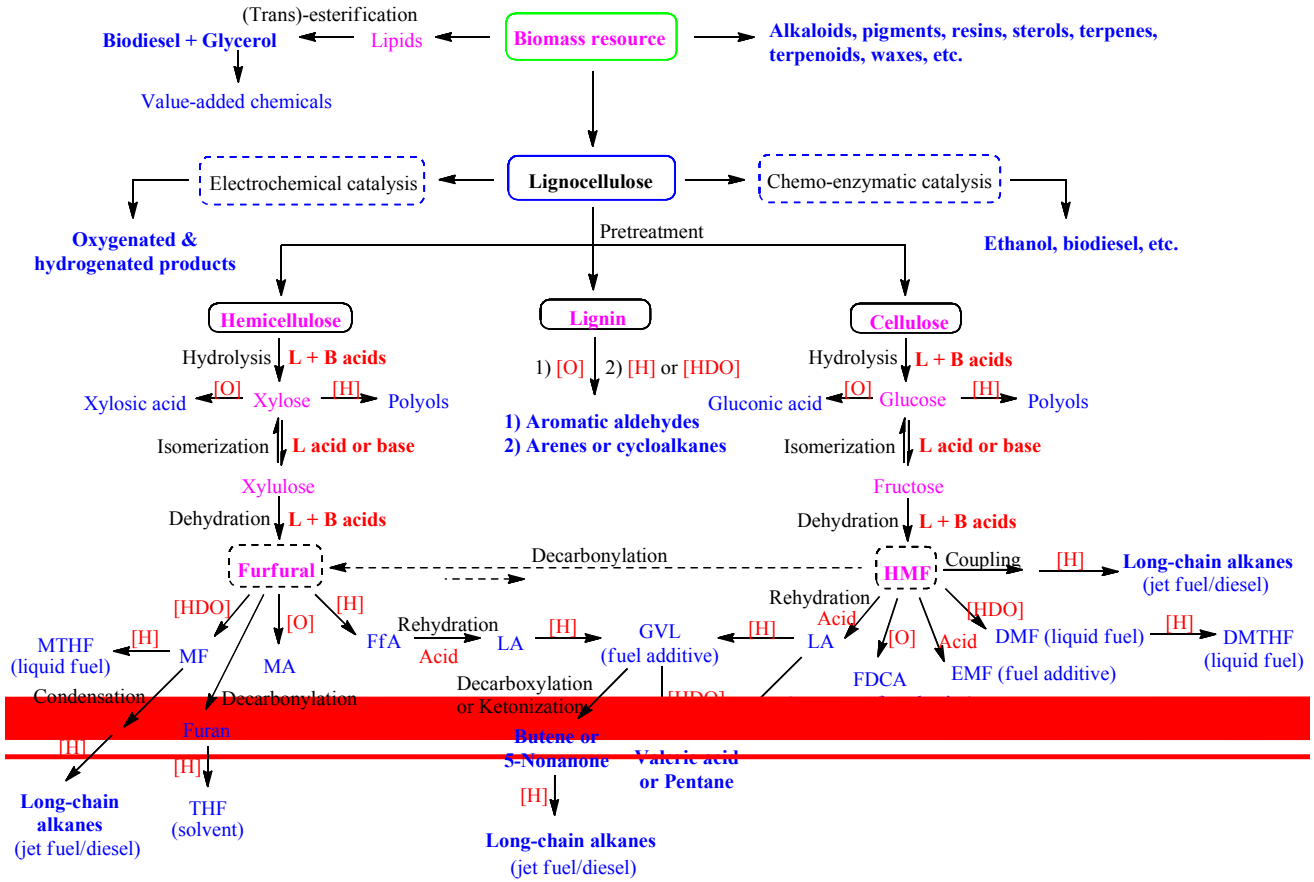
Semi-Flow Reactor for Biodiesel (5L)

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

Image of the pilot *Jatropha* biodiesel plant with output of 20,000 t/year (Kangda Bioenergy Co., Ltd).

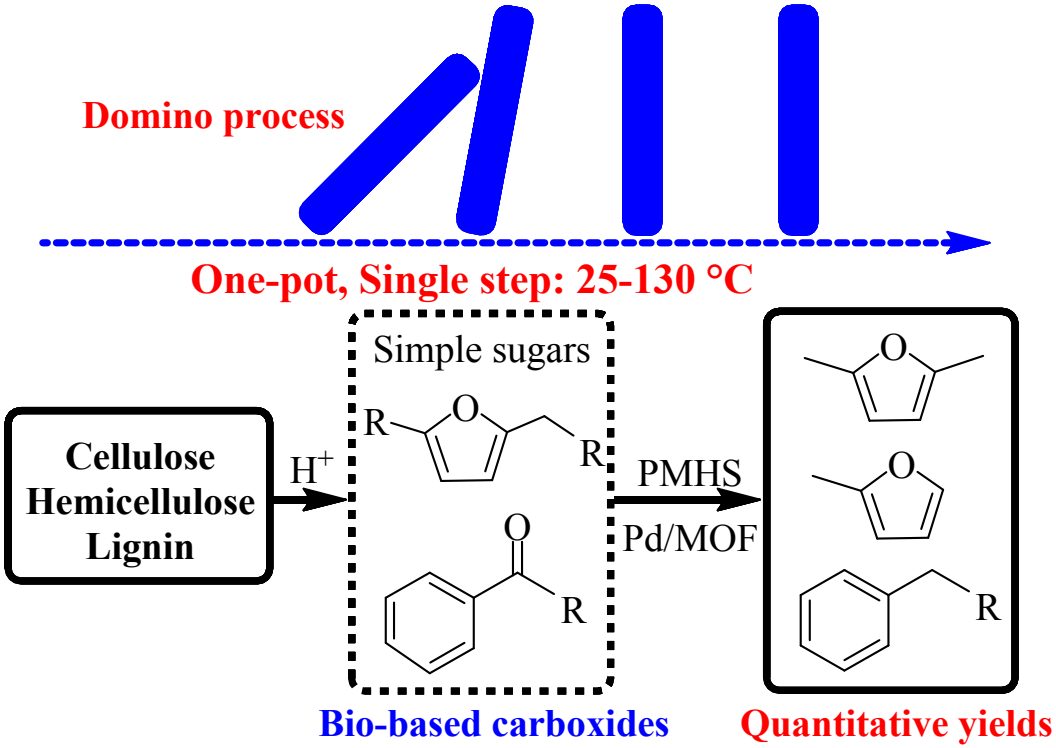
2. Reaction routes for the valorization of biomass with catalytic methods



(L = Lewis, B = Bronsted, [H] = Hydrogenation, [O] = Oxidation, [HDO] = Hydrodeoxygenation, 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-methyltetrahydrahydrofuran, MA = maleic anhydride, THF = tetrahydrofuran, LA = levulinic acid, GVL = γ-valerolactone)

H Li, **Z Fang***, et al. *PECS* 55, 98–194 (2016).

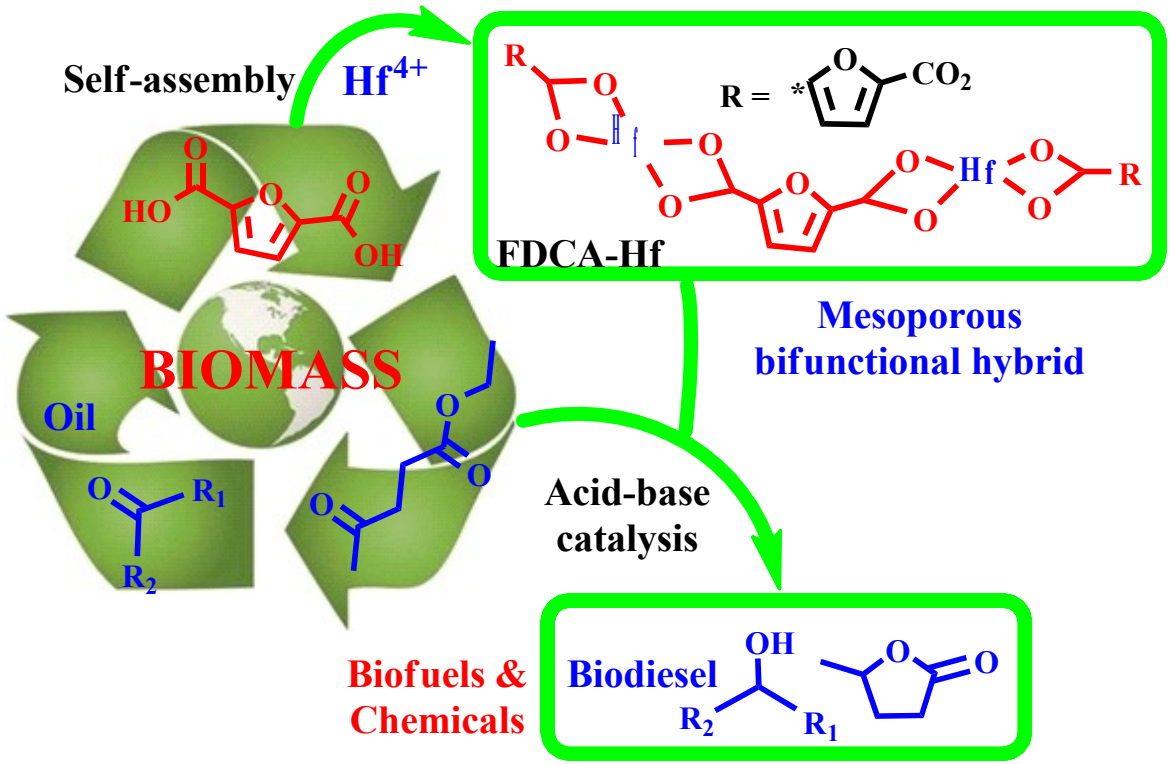
Direct production of engine fuels from sugars at low temperature



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

H Li, W. Zhao, **Z Fang***, et al. *Applied Catalysis B: Environmental*, **215**, 18-27 (**2017**).

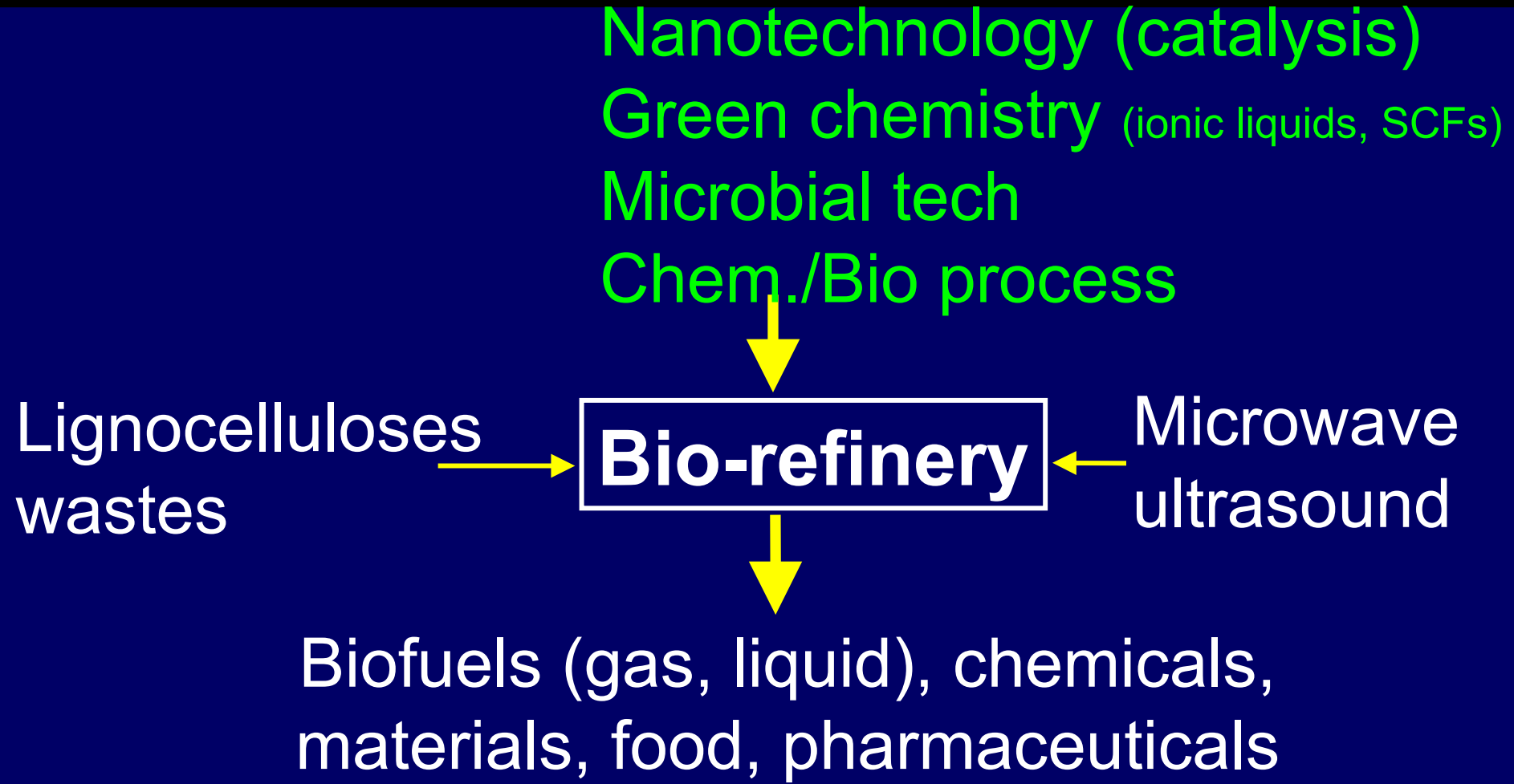
Direct production of engine fuels from sugars at low temperature



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).**

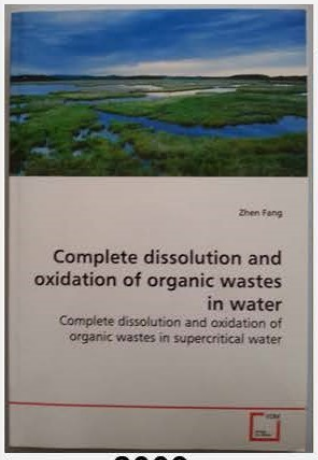
Interdisciplinary Combination



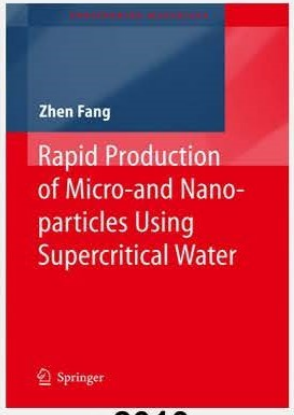
Integration the 4 areas (nano, green chem., microbial and eng.) to effectively refine biomass wastes

Recent published book (2009-now)

258k downloads



2009



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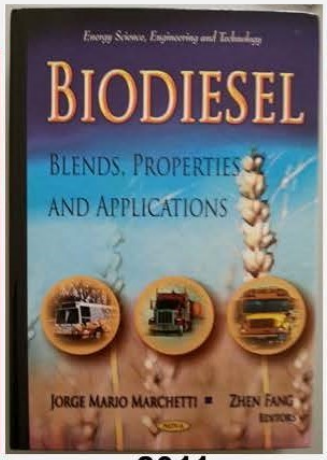
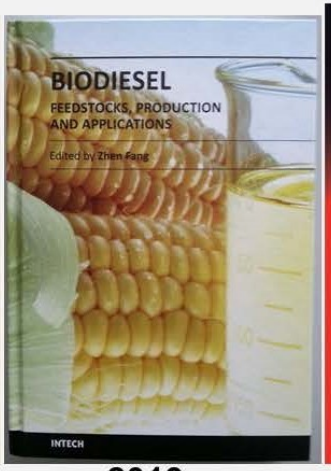
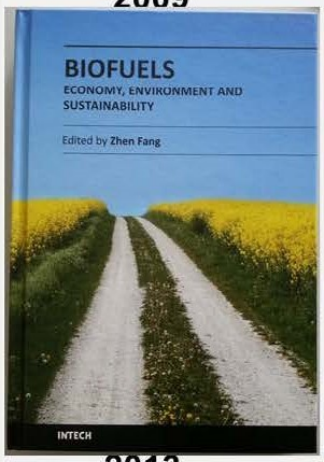


2011



2013

2013



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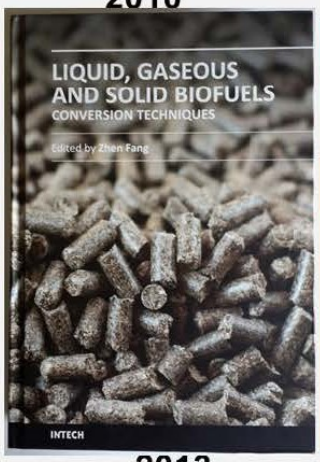

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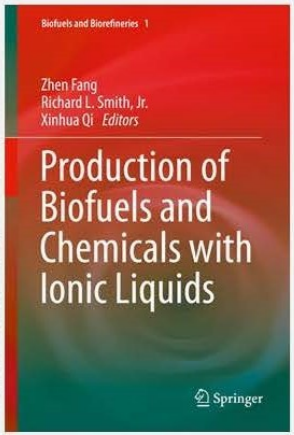

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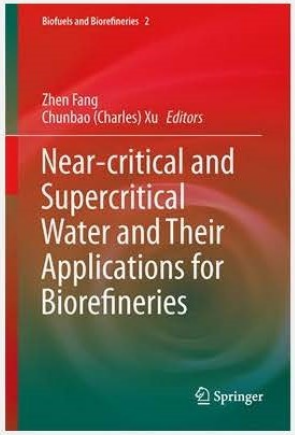

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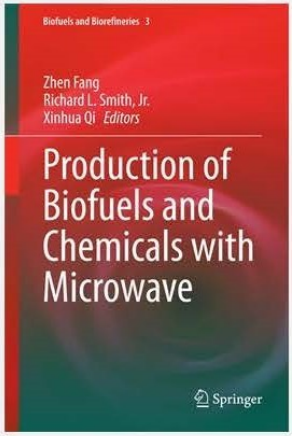

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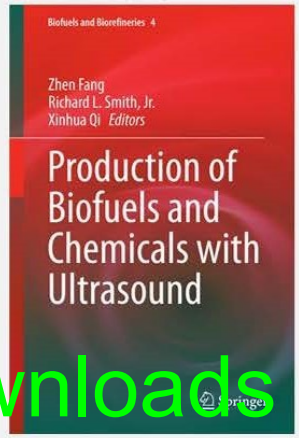

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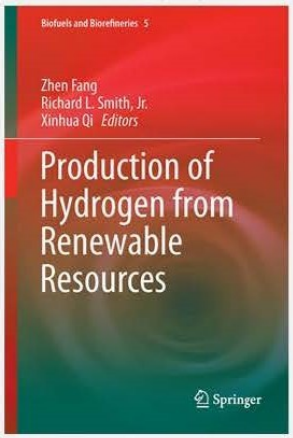

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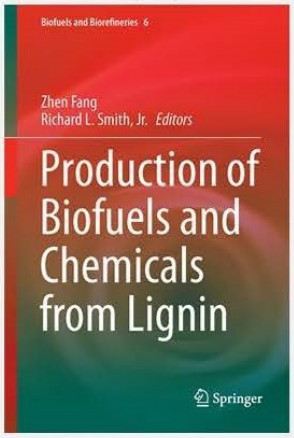

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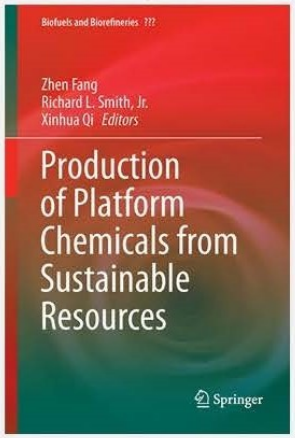
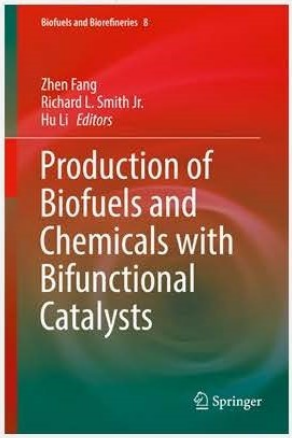


2017



2017