Heterogeneous catalysis for biodiesel production from 
Jatropha curcas oil.
Abebe K. Endalew, Yohannes Kiros, Rolando Zanzi
Department of Chemical Engineering & Technology, KTH-Royal Institute of Technology,
S-100 44 Stockholm, Sweden

1. Introduction

Vegetable and inedible oils similar to diesel fuel have high heating value (HHV). However, their high viscosity and density as well as low volatility make them difficult to be used directly in compression-ignition engines due to the formation of carbon deposits causing injector fouling and failure. Therefore, vegetable/inedible oils also known as triglycerides have to be converted by transesterification to biodiesel or fatty acid methyl esters (FAME) in order to find application as alternative fuel in engines. The biodiesel obtained in such a way can be used either in its pure form or may be blended with petroleum diesel in engines. Currently, most of the biodiesel produced on commercial basis is dependent on the homogeneous reactions of triglycerides with methanol by the alkali-catalyzed reaction according to the following consecutive scheme:

\[ \text{Triglycerides + ROH} \leftrightarrow \text{diglycerides+FAME} \]
\[ \text{Diglycerides + ROH} \leftrightarrow \text{monoglycerides+FAME} \]
\[ \text{Monoglycerides+ ROH} \leftrightarrow \text{glycerol+ FAME} \]

A new approach using heterogeneous catalysts has attracted much attention in recent years for the production of biodiesel. Many different heterogeneous catalysts have been developed and tested at the laboratory scale for the transesterification reactions. Unlike homogeneous catalysts, heterogeneous catalysts can be regenerated with better separation of the final product, are cheap, are environmentally benign and are not considerably affected by the presence of free fatty acids (FFA) and/or water.

2. Background

Jatropha curcas is considered and viewed by many to be the main source of biodiesel in the future. Besides its oil content of up to 40%, its main advantages are also the following:

- Fast-growing, easily propagated by cuttings
- Pest resilient
- Non-competitive to other crops
- Grows in arid and semi-arid areas
- Grows and lives up to 8m and 50 years
- Prevents soil erosion/land reclamation
- Not browsed by animals
- Used as medicinal plant
- A yield of 5-10 ton/ha/year
- Oil increases trade among poor and rich countries
- Alleviates balance of payment and dependency on oil import

3. Experimental

A set of various heterogeneous catalysts were tested for the transesterification reaction of jatropha curcas oil (JCO). Catalysts of CaO and lithium doped CaO, La2O3 supported on ZnO and Al2O3 were prepared at high calcination temperatures. An acid solid catalyst of the type Fe2(SO4)3 was also used together with the catalysts. A three-necked batch reactor with a condenser was employed for the reaction conditions of 60 °C of reaction temperature, 3 hrs of reaction time, 6:1 molar based alcohol to oil ratio, 5 wt.% catalyst (based on the amount of oil) and an agitation speed of 300 rpm. BET-measurements of the catalysts were obtained by ASAP-3000 under N2 adsorption isotherms, while the reaction products were recorded using a GC (Agilent 6890) with flame ionization detector (FID).

4. Results

Acid-base titration measurement of jatropha curcas oil gave a 17 mg KOH/g(oil) (ca 9 wt.% free fatty acid) while the commercial RSO (rapeseed oil) used in this study was found to have a FFA content of less than 1 mg KOH/g (0.53 wt.% FFA). The density of JCO used in this work was measured to be 0.915 g/cm3 while commercially available rapeseed oil has 0.89 g/cm3. Kinematic viscosity of JCO and RSO was measured at room temperature and was found to be 38.4 and 37.5 cSt, respectively.

CaO is the best known solid base catalyst for transesterification of low FFA content oils. It is relatively cheap and non-toxic. Calcium oxide has been tested for transesterification of many vegetable oils such [19]. However, like most alkaline catalysts, soap formation is the main problem consuming and deactivating the catalyst for transesterification of high FFA content vegetable oils. The CaO having a surface area of 2m2/g was tested for its activity in the transesterification of JCO and only 18% FAME yield was obtained and much soap was formed as shown in Fig. 1.

Li-CaO catalyst was tested for transesterification of JCO and RSO. A complete conversion was possible for RSO and a conversion of 66.4% was obtained for JCO. Significant amount of soap was formed for JCO transesterification due to the high FFA content of the oil. The yield showed a better performance of Li-CaO for transesterification of high FFA content oil compared to pure CaO catalyst. Fig. 2 shows the yield of biodiesel from JCO and RSO by Li-CaO and a comparison biodiesel from RSO by CaO. La2O3-ZnO has shown a conversion of 30.1% to biodiesel for the JCO. However, unlike the CaO and Li-CaO catalysts, soap formation was not noticed using this catalyst.

Fig. 1. CaO as catalyst for JCO
Fig. 2. Li-CaO catalyst a) biodiesel from JCO b) biodiesel from RSO c) biodiesel from RSO by CaO

A single step simultaneous reaction system where esterification takes place by Fe2(SO4)3 and transesterification by the solid base showed high conversions as shown in Fig. 3. Ratios of M:Fe2(SO4)3 (there M is either CaO, Li-CaO) of 3:1 and 2:1 were used and total conversion was obtained in the latter case.

Fig. 3. FAME yield in single-step esterification and transesterification of JCO

5. Conclusions

- CaO, Li-CaO and La2O3-ZnO have shown biodiesel conversions of 18%, 66.4% and 30.1%, respectively for oil from jatropha
- The same catalysts have also shown complete conversions to biodiesel for oil from rapeseed
- Combination of solid base and solid acid catalysts resulted in total conversions except for La2O3-ZnO, which was ca. 40%
- Reuse of the catalysts is possible by limiting the carbonisation of the base solid catalysts