A preliminary study of acid catalyzed transesterification of a Jatropha-like bio-oil

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ARTICLE INFO

ABSTRACT

This project aimed to develop a better understanding of acid catalyzed transesterification using various catalysts and evaluating the biodiesel reaction yield using simulated Jatropha oil made from Sesame seed oil, which has a similar composition. Five zeolites were compared: Y, 13-X, beta, mordenite, and ZSM-5. Non-catalyzed and homogeneously catalyzed reactions, with H_2SO_4, also were evaluated. Zeolites that were not in the hydrogen form were ion-exchanged, and were then analyzed by Energy-Dispersive X-Ray spectroscopy. Three alcohol-to-oil ratios were tested at atmospheric pressure and $T = 115\ °C$ for each catalyst in order to determine the influence of this parameter. All experiments were conducted in an airtight autoclave with butan-1-ol in order to obtain a biofuel whose cetane index was higher than regular petroleum-based diesels. Among the zeolites tested, the Y-type was the most efficient solid acid catalyst, and the final conversion reached after 3 h with a butanol-to-oil molar ratio of 15:1 was around 61%.

1. Introduction

Sustainable energy production has become a high priority for many countries. Biofuels are one of the most promising solutions being researched to address this urgent problem. In particular, using transesterified Jatropha curcas L. oil appears to be a promising method of producing biofuels due to several properties of the plant, such as the high oil yield of its seeds and the fact that it does not compete with food crops [1]. While Jatropha curcas L. cultivation may not make economic sense in all geographic locations, it grows well in the Caribbean climate, and is predicted to have promise for success in places like Haiti.

This perennial species is a seed-bearing shrub or small tree (the biggest specimens can reach 6 m) that has the quality to adapt and grow under numerous climatic conditions from dry tropical to moist subtropical or wet tropical forest. It can support rainfalls from 200 mm y^{-1} to 2380 mm y^{-1}, 200 mm y^{-1} being sufficient for seed production. It does best in drier tropical areas and is undemanding on soil, being well adapted to poorer soils [2]. Jatropha curcas fruits are typically 2.5 cm long, ovoid, black and have 2 or 3 sections. Seed production goes from 0.4 to over 12 t $ha^{-1}\ y^{-1}$. Kernels and seeds have high oil content. On average, 100 kg of whole seeds (hulls/husks + kernels) contain 28—30 kg of oil [1].

This oil comes from a plant whose characteristics make it a strong candidate for the production of biodiesel on a large scale. In addition to avoiding the competition with food crops, the plant has been proven to have high oil content and to be able to grow under harsh climate conditions. The other parts of the plants (mainly the fibrous material from the wood-type by-products) can also be taken advantage of in the production of other types of fuels and extra-energy [3]. Finally, the

biodiesel produced from raw Jatropha oil does not require any modification of engines and can be used in the same way as petroleum-based diesel [4].

Acid catalyzed transesterification prevents soap formation (saponification) and emulsification, which can be observed using basic catalysts when the agricultural oil has a high free fatty acid content, as Jatropha oil does [5—7]. The use of a solid catalyst makes the separation and purification of the final products steps easier to implement in comparison to catalysis in homogeneous conditions, since separations can be by physical methods [7]. However, the efficiency of zeolites in the heterogeneous transesterification reaction of vegetable oil is not well-known yet and may vary with the structure of the zeolite catalyst used. While details are not complete, it is thought that heterogeneous catalysts will prove to be more efficient than homogeneous catalysts [7].

Molecular sieve zeolites are crystalline alumino-silicates with metal atoms (Si, Al, …) in tetrahedral coordination with four shared O atoms. Consequently, $Si-O_4$ tetrahedra are charge neutral, while $Al-O_4$ tetrahedra carry a net negative charge in the crystalline framework. These negative charges are balanced by exchangeable cations, usually Na^+ as synthesized. Other cations may be ion exchanged to replace the sodium, giving zeolites use as in-situ ion exchangers in detergents to scavenge Mg^{2+} and Ca^{2+} water-hardening ions. Protons provide catalytic acidity when exchanged in as NH_4^+; calcining drives off NH_3 gas, leaving a proton, H^+, to balance the negative charge in the structure. The Si/Al ratio in zeolites can vary between 1.0 and infinity. High-Alumina zeolites are hydrophilic, while high-Silica zeolites are increasingly hydrophobic.

Zeolite structures can be tailored in different ways and their catalytic properties adjusted to reach particular goals. Usually used as ion scavengers in detergents or in catalytic processes in the petroleum industry, their uses have expanded to include a large variety of chemical reactions and adsorption of organics from water. The particular structures exhibited by zeolites are often an advantage in a way that they enable the catalysis of certain reactions, preventing others from occurring at the same time which makes the process very specific. On the other hand, this great specificity can be a drawback if the zeolite is not perfectly adapted to the type of reaction it is supposed to catalyze. As a consequence, yields of transesterification reactions of vegetable oils were not found as satisfying as with other types of catalysts. Sasidharan and Kumar [8] observed less than 30% of conversion for conversions of beta-keto ester with H-ZSM-5, while Brito et al. [9] observed only 26% conversion of waste cooking oil using H-Mordenite. The same reaction implemented by Sasidharan and Kumar with an H—Y zeolite exhibited a yield over 85%. Kiss et al. [10] obtained a 26% conversion using H-mordenite and a waste cooking oil; Shu et al. [11] used H-beta zeolite and achieved 36% conversion of a soybean oil. Thus, the type of zeolite and its properties are important factors in the transesterification reactions.

In this study, we report the results of acid catalyzed transesterification of a simulated Jatropha oil using five solid zeolites (13-X, Y, mordenite, beta, and ZSM-5), and a liquid phase acid catalyst (H_2SO_4), compared to the un-catalyzed

reactions. Reactions were carried out at 115 °C with butan-1-ol to oil ratios of 3:1, 6:1, and 15:1.

2. Materials and methods

2.1. Materials

Since a supply source for Jatropha curcas oil was difficult to locate, and purchase and transportation costs were rather high, a jatropha oil-simulant was created. The fatty acid profiles of Jatropha and Sesame oils were reported to be quite similar, as shown in Table 1 [12], so raw sesame oil was obtained from Kevala International, LLC (Rowlett, TX) as a starting point to develop a Jatropha simulant. A GC/MS was used to characterize the raw sesame oil and compare to the fatty acid content reported to be in Jatropha oil. On the basis of the differences, the amounts of the fatty acids added to the raw sesame oil are reported in Table 2. The raw sesame oil with the added fatty acids was the starting bio-oil used in the subsequent transesterification experiments. The simulated oil had a free fatty acid content almost identical to that of Jatropha oil.

Five molecular sieve zeolites were used in the transesterification experiments: 13-X and Y (Sigma Aldrich), beta, mordenite, and ZSM-5 (Zeolyst International). All of the zeolite samples were powders approximately 2.0 μm in size, except the ZSM-5 sample, which was in grains of approximately 0.4 mm with an alumina binder. The zeolites Y, beta, and mordenite were known to be in the H^+, or acidic, form, and so no further treatment steps were required for those. The ZSM-5 was in the NH_4+ form, and so was calcined at 500 °C to drive off NH_3, leaving a proton to balance the charge in the structure. Zeolite 13-X was in the Na^+ form, and so was ion-exchanged batchwise four times to replace Na^+ with NH_4^+ cations, after calcining at 500 °C to eliminate any adsorbed impurities. A 1.0 mol L^{-1} solution of NH_4Cl was prepared to use as the ion exchange medium. 10 g of the calcined zeolite sample was placed in a 2000 ml 3-neck flask with a reflux condenser, into which 1000 ml of the ion exchange solution was also introduced. These ion exchanges were conducted for 40 min each, at 60 °C. The fourth ion exchange step was followed by calcination at 500 °C for 3 h to drive off NH_3 gas, leaving the anionic sites in the crystal frameworks compensated by a proton, or $H+$, to provide acidity. EDX spectroscopy of the initial and final zeolite samples demonstrated that the Na^+ ions had been substantially reduced from the samples. In the 13-X sample, the atom % of Na^+ dropped from an initial value of 9.90% to 0.85%.

The choice of alcohol to use in the transesterification reaction was considered. Alcohols with 6 carbons or more, as

Table 1 — Fatty acid % in sesame oil and Jatropha oil [11].		
	Sesame oil	Jatropha oil
Palmitic (C16:0)	8 — 12	11 — 16
Stearic (C18:0)	4 — 7	6 — 15
Oleic (C18:1)	35 — 45	34 — 45
Linoleic (C18:2)	37 — 48	30 — 50