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Biodiesel Production by Integrated Reactive-Separation Design

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Abstract

The properties of biodiesel as renewable fuel, as well as the problems associated with its conventional production processes are outlined. A novel sustainable process based on catalytic reactive distillation is proposed as alternative. The pros and cons of manufacturing biodiesel via fatty acid esterification using metal oxides as solid acid catalysts are investigated. The experimental findings are used for designing a biodiesel plant with a production rate of 10 kt/year.

Keywords: reactive distillation, solid acids, green catalysts, sustainable fuels.

1. Introduction

The increasing energy demand makes the implementation of sustainable fuels a crucial issue worldwide. Biodiesel became very attractive due to its renewable sources, good performance and many environmental benefits. It can be produced from vegetable oils, animal fat or even recycled grease. Biodiesel has several advantages over petroleum diesel: it is safe, renewable, non-toxic and biodegradable; it contains no sulfur and is a better lubricant.[1] Unlike petroleum diesel, biodiesel consists of a mixture of mono-alkyl esters of long chain fatty acids. Despite the chemical differences these two fuels have similar properties (Table 1). Biodiesel brings also additional benefits to the society: rural revitalization, less global warming, energy supply security. Its production is increasing rapidly as biodiesel can be distributed using today's infrastructure.

Table 1. Properties of biodiesel vs. petroleum diesel.

Fuel property	Diesel	Biodiesel
Fuel standard	ASTM D975	ASTM D6751
Fuel composition	C_{10}-C_{21} HC	C_{12}-C_{22} FAME
Kinetic viscosity, mm^2/s (at 40 °C)	1.3 – 4.1	1.9 – 6.0
Specific gravity, kg/l	0.85	0.88
Boiling point, °C	188 – 343	182 – 338
Flash point, °C	60 – 80	100 – 170
Cloud point, °C	−15 to 5	−3 to 12
Pour point, °C	−35 to −15	−15 to 10
Cetane number (ignition quality)	40 – 55	48 – 65
Stoichiometric Air/Fuel Ratio (AFR)	15	13.8
Life-cycle energy balance (energy units produced per unit energy consumed)	0.83 / 1	3.2 / 1

An important characteristic of diesel fuels is the ability to auto-ignite, quantified by the cetane number (cetane index). Biodiesel not only has a higher cetane number than petroleum diesel, but also a higher flash point meaning better and safer performance. Blends of biodiesel and petroleum diesel are designated by a 'B' followed by the vol.% of biodiesel. B5 and B20 – the most common blends – can be used in unmodified diesel engines that power conventional cars.

The presence of oxygen in biodiesel (~10%) improves combustion and reduces CO, soot and hydrocarbon emissions, while slightly increasing the NO_x emissions. Figure 1 shows the biodiesel vs. petroleum diesel emissions, as well as the amount of CO_2 per distance produced by various fuels. Remarkably, biodiesel is the only alternative fuel currently available with an overall positive life cycle energy balance (Figure 2, left).

Nowadays, there are five major routes to produce biodiesel: 1. direct use and blending of straight vegetable oil, 2. use of microemulsions with short-chain alcohols, 3. thermal cracking (pyrolysis) of vegetable oils, 4. trans-esterification of tri-glycerides (TG) catalyzed by bases, acids, or enzymes, 5. esterification of fatty acids with alcohols, using liquid (H_2SO_4) or solid acid catalysts.[1-3]
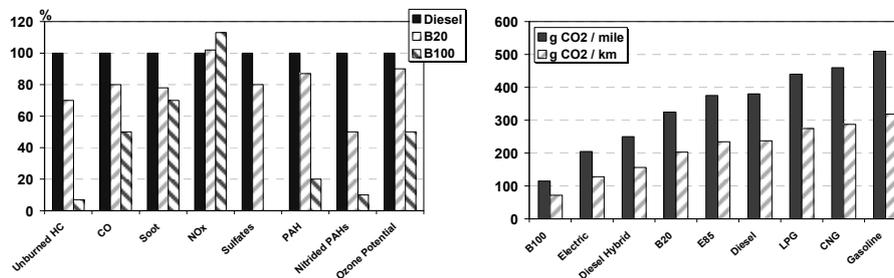
Figure 1. Biodiesel vs. petroleum diesel emissions (left). Comparison of CO_2 emissions (right).
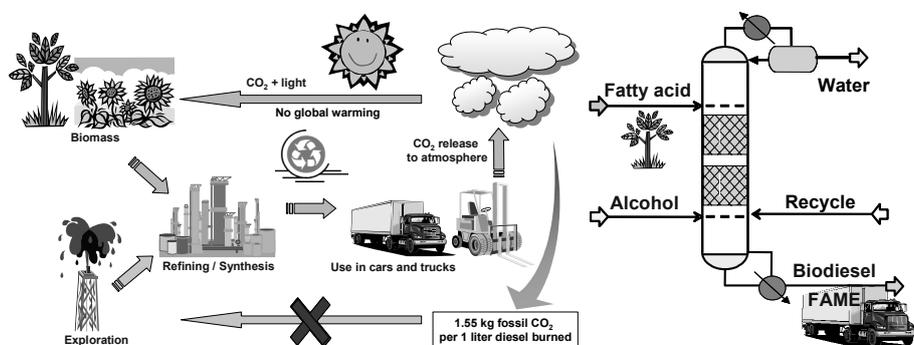
Figure 2. Life cycle of diesel vs biodiesel (left). FAME production in RDC (right).

2. Problem Statement

Fatty acid methyl esters (FAME) are currently manufactured by either trans-esterification using liquid Na/KOH catalyst, or batch esterification of free fatty acids (FFA) using H_2SO_4 as catalyst. The catalyst removal is essential due to the EU restrictions on sulfur content in diesel fuels (< 15 ppm).

The problem is that these catalysts require neutralization and an expensive multi-step separation that generates salt waste streams, thus making biodiesel an attractive but still costly alternative fuel. To solve these problems, we replace the homogeneous catalyst with solid acids[2] and develop a sustainable esterification process based on catalytic reactive distillation (Figure 3, right).

Previously, we have screened a large number of zeolites, heteropoly-compounds, metal oxides, ion-exchange resins, and carbon-based solid acids.[3] In this work, we focus on the application of metal oxides catalysts (based on niobia, zirconia, titania and tin oxide) in an integrated reactive-separation design that is able to shift the chemical equilibrium to completion and preserve the catalyst activity by continuously removing the products. The integrated design is based on the experimental findings and rigorous simulations in Aspen Plus™.

3. Experimental work

At industrial scale, a solid acid esterification catalyst must fulfil several conditions that seem trivial on the laboratory scale. It should have high activity and selectivity to avoid by-products formation, it should be water-tolerant to avoid catalyst deactivation and stable at relatively high temperatures to achieve high reaction rates. Additionally, it must be an inexpensive material that is readily available. Considering these conditions and previous literature reports, we investigated metal oxides with strong Brønsted acid sites and high thermal stability. Based on the literature reviews and our previous experimental screening we focus here on metal oxide catalysts based on Zr, Ti, and Sn.
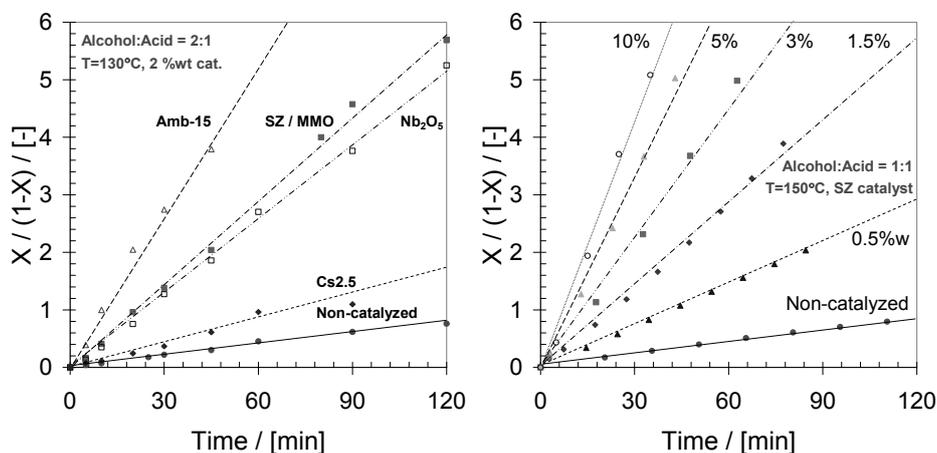
Figure 3. Esterification of dodecanoic acid: (left) at 130°C using solid acid catalysts (2 wt%), (right) non-catalyzed and catalyzed (0.5-10 wt% SZ catalyst)

Sulfated zirconia (SZ) outperformed other solid acids, and by increasing the amount of catalyst the reaction rate can be further increased (Figure 3). SZ showed good thermal stability, high activity and selectivity for the esterification of fatty acids with a variety of alcohols ranging from C_1 to C_8. In our experiments using metal oxides as catalysts, no by-products were observed under the reaction conditions, by GC analysis. Considering these promising results, we tested also sulfated titania and tin oxide. These catalysts performed slightly better than SZ, showing increased acid conversion (Figure 4). However, sulfated zirconia is less expensive and it is readily available at industrial scale.
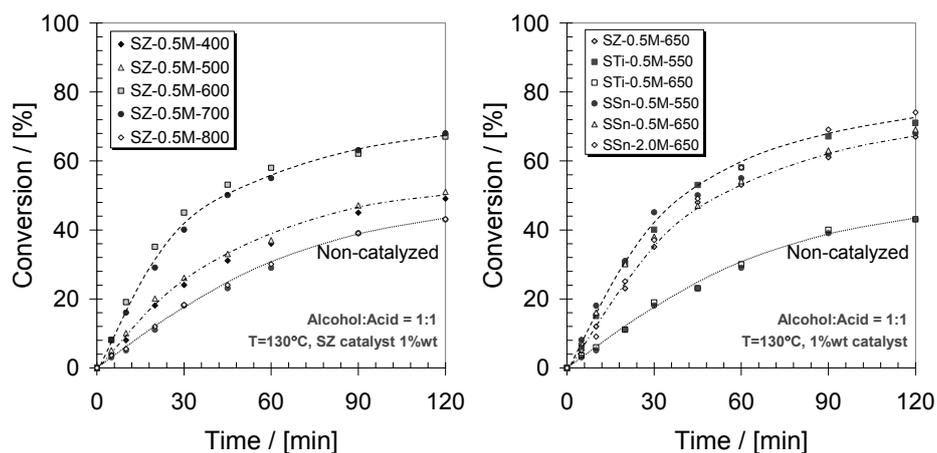
Figure 4. Reaction profiles using: sulfated zirconia catalyst calcinated at 400-800 °C (left), and sulfated zirconia, titania and tin oxide catalysts (right)
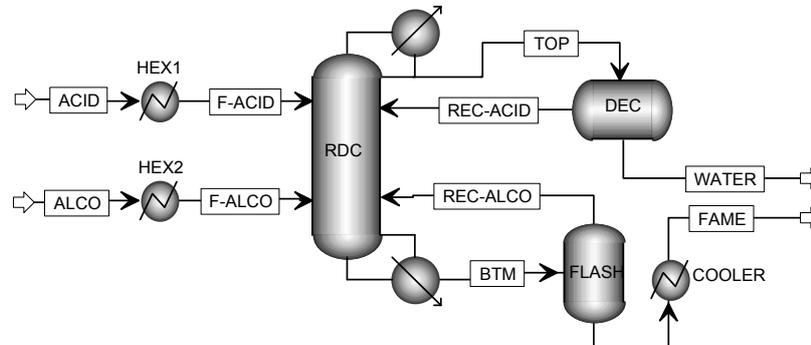
Figure 5. Flowsheet of biodiesel production based on catalytic reactive distillation.

4. Results and disscussion

The design is based on a reactive distillation column (RDC). An additional flash and decanter are used to guarantee the high purity of the products (Figure 5). The reactive distillation column is operated in the temperature range 70–210 °C, at ambient pressure. Out of the 15 stages of the reactive distillation column, the reactive zone is located in the middle of the column (stages 3-10). The fatty acid is fed on top of the reactive zone while methanol as saturated liquid is fed below the reactive zone. The mass balance is given in Table 2, while the composition, temperature and reaction rate profiles in the RDC are plotted in Figure 6.

The reflux ratio in the reactive distillation column is relatively low (0.1 kg/kg). A higher reflux ratio is detrimental as it brings back water by-product into the column, thus decreasing the fatty acids conversion by shifting the equilibrium back to reactants. High purity products are possible, but due to the thermo-stability and high boiling points of FAME (i.e. high temperature in the reboiler) this should be avoided. By allowing ~0.2% of alcohol in the bottom stream, the reboiler temperature in the RD column can be limited to ~200 °C.

Table 2. Mass balance of the biodiesel production process bassed on reactive-distillation.

	F-ACID	F-ALCO	BTM	REC-ALCO	FAME	TOP	WATER
Temperature K	418.1	338.6	480.4	480.4	303.1	372.8	323.1
Mass Flow kg/hr							
METHANOL	0	188.631	1.883	0.391	1.492	0.011	0.011
ACID	1167.607	0	0.144	0	0.144	0.11	0.015
WATER	0	0	0.005	0.001	0.003	104.988	104.986
ESTER-M	0	0	1249.195	0.834	1248.361	0.01	0
Mass Frac							
METHANOL	0	1	0.002	0.319	0.001	0	0
ACID	1	0	0	0	0	0.001	0
WATER	0	0	0	0.001	0	0.999	1
ESTER-M	0	0	0.998	0.68	0.999	0	0
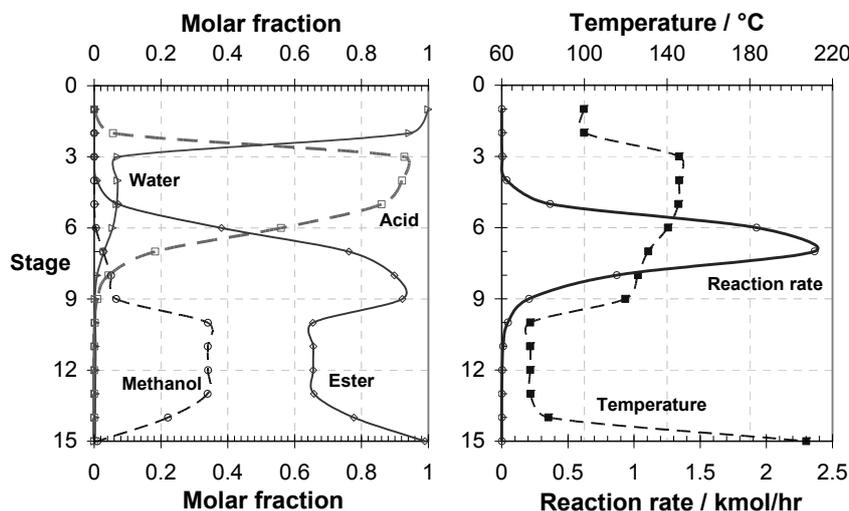
Figure 6. Profiles in RDC: liquid composition (left), temperature and reaction rate (right).

5. Conclusions

The integrated design proposed in this work is based on catalytic reactive distillation, powered by metal oxides as solid acid catalysts for esterification. This alternative improves the economics and HSE benefits compared to conventional biodiesel processes, and reduces dramatically the number of downstream processing steps. The major benefits of this approach are:
1. Reduced capital and operating costs, due to less units and lower energy use.
2. Increased unit productivity (5-10 times higher than conventional processes)
3. No excess of alcohol required – stoichiometric reactants ratio at RDC inlet.
4. No catalyst neutralization step hence no salt waste streams are produced.
5. Sulfur-free fuel, since solid acids do not leach into the product.
6. High conversions as chemical equilibrium is shifted towards completion.
7. Multifunctional plant suitable for a large range of FFA and TG mixtures.

References

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