



Biofuel synthesis in a capillary fluidized bed



D.C. Boffito*, C. Neagoe, M. Edake, B. Pastor-Ramirez, G.S. Patience

Department of Chemical Engineering, Polytechnique Montréal, C.P. 6079, Succ. CV Montréal, H3C 3A7 Québec, Canada

ARTICLE INFO

Article history:

Received 12 October 2013

Received in revised form

10 December 2013

Accepted 9 January 2014

Available online 12 February 2014

Keywords:

Biodiesel

Transesterification

Heterogeneous catalyst

Fluidized bed

Atomization

ABSTRACT

Hydrotalcite, MgO, CaO and zeolites transesterify canola oil in the gas phase at temperatures above 300 °C and atmospheric pressure. Syringe pumps metered oil and alcohol through a 1/8" tube to the bottom of a 7 mm "capillary"-fluidized bed. Argon gas entered the annular region of the bed through a sintered glass frit as supplemental fluidizing gas. Oil conversion was complete with excess methanol in the feed. Contact times were less than 0.3 s and the weight-hourly space velocity was on the order of 15 h⁻¹ (0.15 ml min⁻¹ oil feed rate with 0.5 g of catalyst). As the catalyst deactivates, the oil condenses and the fluidized bed collapses. The zeolite deactivated within 2 min; the hydrotalcite could operate for several minutes; the CaO and MgO operated without interruption for well over 20 min. Periodic oxidation of the catalyst maintained catalyst activity.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Biodiesel is a mixture of fatty acids methyl esters produced from the transesterification of vegetable oil, animal fats and waste greases. Most industrial processes adopt basic homogenous catalysts (NaOH, KOH, NaOCH₃) to transesterify the fat with an alcohol. The free fatty acids that may be present – particularly in waste oils – can be esterified with methanol and H₂SO₄. The current industrial processes are limited by the mass transfer rates and as a consequence, the residence times are long (as much as 8 h or more) and the reactor vessels are large, translating to high fixed and operating costs.

Moreover, the homogeneous catalysts are difficult to recycle and thus become a waste water disposal issue. For these reasons, considerable research efforts have been devoted to heterogeneous (solid–liquid) catalysts. The main advantage of the solid–liquid systems is that the catalyst is readily recycled and less or no waste water is produced. But, still, reaction times may be longer than the liquid–liquid technology. Many different heterogeneous catalysts have been reported for the transesterification: single metal oxides like CaO [1,2]; mixed metal oxides such as Al₂O₃–SnO [3]; zeolites such as NaOx/NaX–Zeolite [4], ETS10 [5], Cs–NaX Faujasite [6];

hydrotalcites [7–9]; immobilized metal salts like KI/alumina [10], Na/NaOH–Al₂O₃ [11], K₂CO₃/alumina [12] and organic solid bases such as alkyl guanidine [13]. The catalysts in each category have acceptable catalytic activity. Heterogeneous catalytic transesterification in batch reactors are reported at temperatures in the range of 60–200 °C. In this study, we present the preliminary data on the gas phase transesterification at temperatures above 400 °C. Biofuel synthesis in a capillary fluidized bed has not been reported in literature previously.

Operating the process in the gas phase addresses the long residence time issue: the oil and methanol may be injected directly into a fluidized bed containing catalyst in the form of a powder operating at elevated temperatures. Temperatures beyond 400 °C are necessary to ensure the vaporization of the reagents, which being in the form of very small droplets react at rates orders of magnitude greater than in the liquid phase – in a matter of seconds. In the case of vegetable oils, temperatures lower than 400 °C form a liquid slurry in the reactor, eliminating the advantages of the fluidized bed reactor, in which the contact catalyst–reagents is very efficient. Another advantage of operating at high temperatures and in vapour phase is given by the possibility of partially condensing the products, resulting in easier separation operations.

When the fluid mixture contacts the catalyst particles, it vapourizes and react at rates orders of magnitude greater than in the liquid phase – in a matter of seconds. The solid catalysts may either be acidic or basic [14] and the bed may operate under vacuum or elevated pressure.

* Corresponding author. Tel. +1 514 3404711x2446; fax +1 5143404159.

E-mail addresses: daria-camilla.boffito@polymtl.ca, daria.camilla.boffito@gmail.com (D.C. Boffito).

2. Experimental

2.1. Catalysts preparation

The Mg–Al hydrotalcite was prepared from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as precursors. A 100 ml aqueous solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (25.38 g), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (12.37 g) was added dropwise to a 100 ml solution containing NaOH (11.88 g), and Na_2CO_3 (9.15 g) and kept under vigorous stirring for 1 h. The precursor solution was then kept at 80 °C for 18 h and cooled to room temperature and then filtered. The residue was washed with hot distilled water several times until the filtrate pH was neutral. The solid was dried in an oven at 60 °C for 12 h. The catalyst was calcined at 500 °C for 3 h (heating rate: 60 °C h⁻¹) in static air. Both $\text{MgO}/\text{Al}_2\text{O}_3$ and $\text{CaO}/\text{Al}_2\text{O}_3$ were synthesized by impregnation of the alumina support through incipient wetness. The loading of the active phase was 10% in both cases. The support, γ -alumina, was 90–150 μm in diameter (Sigma-Aldrich). In a typical procedure, 10 g of Al_2O_3 was loaded into a flask and 10 ml of the precursor solution of the active phase was added dropwise (1–2 drops/min). The concentration of the solution was 4.45 M for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 4.96 M for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The support was impregnated for 24 h in a rotavapor at 25 °C. The temperature was then raised to 50 °C and the water evaporated at 0.5 bar for 24 h. The catalyst was dried at 80 °C in an oven overnight and calcined at 500 °C for 3 h (120 °C min⁻¹ in static atmosphere). The powder was sieved and the fraction between 90 μm and 150 μm was retained for the experiments. The Fluidized Catalytic Cracking (FCC) catalyst was a commercial SiO_2 - Al_2O_3 ZSM5 zeolite.

2.2. Catalysts characterization

Nitrogen multipoint isotherms were measured at 77 K using an Autosorb-1 (Quantachrome Instruments). All samples were degassed at 423 K overnight under vacuum. The specific surface area (SSA) was calculated with the standard multi-point Brunauer–Emmett–Teller (BET) method. The particle size distribution (PSD) was quantified by a Laser Scattering PSD Analyzer LA-950 (Horiba). The crystallinity was measured with a Philipps X'pert diffractometer at room temperature with an angle of incidence of 0.5°. The XRD patterns were recorded using $\text{Cu K}\alpha$ (1.5406 Å) radiation at 50 kV and 40 mA. The diffraction angle was scanned between 20° and 90°, and a divergence slit of 1°.

2.3. Capillary-fluidized bed and catalytic tests

All experiments were conducted in a 7 mm quartz tube containing catalyst operated in the bubbling fluidized bed regime. Canola oil and methanol were metered to the reactor by syringe pumps (Fig. 1). An inert carrier gas – Ar – helped atomize the liquids that were fed to the bottom of the fluidized bed of catalyst through a 1/16 in SS tube. The distributor of the fluidized bed was made of a 20 mm thick layer of glass wool. The sparger tube passed through the glass wool and protruded into the fluidized bed by approximately 3 mm. Ar and Ar/O₂ were fed to the annular region either to supplement the fluidization of the catalyst or to regenerate the catalyst. Ar was fed to the top of the reactor, into the freeboard region, to cool the product gases and thereby minimize gas phase cracking. A thermocouple entered from the top of the reactor and extended down into the bed to monitor temperature. The flow rate of Ar fed to the top of the tube was maintained at 12 ml min⁻¹ (STP) with a needle valve. The fluidization gas was maintained at 40–60 ml min⁻¹ (STP) depending on the catalyst by an MKS mass flow controller. Four catalyst samples were tested: MgO, hydrotalcite, FCC and CaO (Table 1). The hydrotalcite and FCC (Fluidized

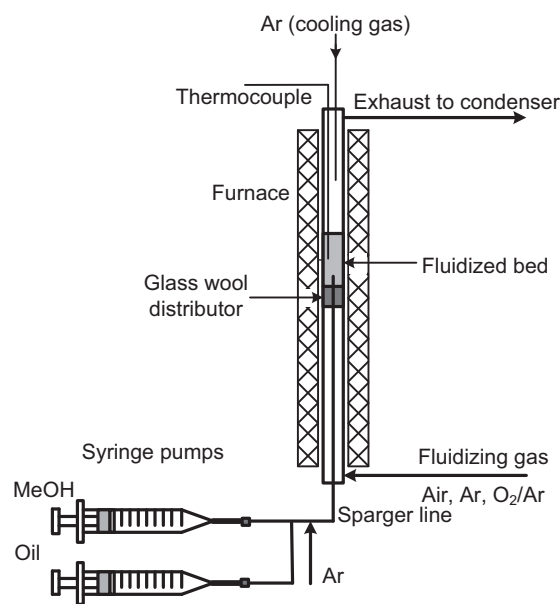


Fig. 1. Fluidized bed schema.

Catalytic Cracking) catalyst had the highest minimum fluidization velocity and thus the fluidization gas in the annular region was maintained near 60 ml min⁻¹ while the MgO and CaO supported on alumina had the lowest minimum fluidization velocity and hence its flow rate was maintained at 40 ml min⁻¹. The Ar flow rate to the sparger was maintained at 12 ml min⁻¹ by a second MKS mass flow controller. Oil flow rates between 0.05 ml min⁻¹ and 0.15 ml min⁻¹ were tested with MeOH:oil ratios ranging between 5:1 and 1:1. The product gases exited the top of the reactor into a 1/8 in SS tube in which the heavier compounds condense and were subsequently collected in a graduated clear flask. The EN 14103-2011 standard was adopted to quantify the methyl esters. The capillary GC column DBWax was used in a GC Varian (CP-3800) operating with a temperature ramp from 60 °C to 200 °C, heating rate of 10 °C min⁻¹ and then up to 240 °C with a heating rate of 5 °C min⁻¹. He was used as a carrier gas at 70 kPa. The BD yield, expressed as a mass fraction of FAME, was calculated according to:

$$C_{BD} = \frac{\Sigma A - A_{C19}}{A_{C19}} \frac{C_{C19} V_{C19}}{m} \quad (1)$$

where ΣA is the total peak area of the FAME, A_{C19} is the peak area corresponding to methyl nonadecanoate; C_{C19} is the concentration (mg ml⁻¹), of the methyl nonadecanoate solution used as standard; V_{C19} is the volume (ml) of the methyl nonadecanoate solution; m is the mass, in mg, of the sample.

Samples of the non-condensable gases were also measured by GC–MS. At times, the gas phase was also monitored on-line with a ThermoStar GSD 300T mass-spectrometer (Pfeiffer).

Table 1
Catalytic tests.

Catalyst	MgO/Al ₂ O ₃	CaO/Al ₂ O ₃	Mg–Al hydrotalcite	FCC catalyst
Q_{oil} , ml min ⁻¹	0.05	0.1	0.05	0.05
Q_{MeOH} , ml min ⁻¹	0.05	0.1	0.1	0.05
$Q_{\text{fluidization gas}}$, ml min ⁻¹	40	40	60	60
t , min	16	32	90	34
T , °C	450	450	450	500
Yield, %	24	21	63	50

Download English Version:

<https://daneshyari.com/en/article/53971>

Download Persian Version:

<https://daneshyari.com/article/53971>

[Daneshyari.com](https://daneshyari.com)