



Biodiesel production under mild reaction conditions assisted by high shear mixing



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ABSTRACT

In this work, a sustainable way for biodiesel production is presented. It consists in performing the transesterification reaction by a high shear mixing assistance at room temperature and atmospheric pressure. The process involves the generation of a microemulsion between the reactants (methanol and soybean oil) in the presence of a homogeneous catalyst. The effect of the catalyst nature and amount, dispersion rate and time, and methanol:oil ratio were investigated. In order to verify a wide applicability, other vegetable oils such as canola, sunflower, corn and olive were evaluated as well. The required energy consumption using the high shear mixing assistance was smaller than that consumed in a traditional method. The results showed that this method is suitable for other vegetable oils using low quantities of methanol, catalyst, and short reaction times (less than 1 min). Moreover, the use of costly equipment and spacious facilities are avoided. Using the herein described methodology, a quantitative conversion was achieved.

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1. Introduction

Global energy crisis is becoming a controversial fact regarding to a rapid population growth that requires an increased safe energy and less fossil fuel resources consumption. Renewable energy sources are gaining widespread attention due to the current environment issues related to emissions of toxic and greenhouse gases (generated mainly from the combustion of fossil fuels) such as global warming and ozone layer depletion [1].

In order to combat the climate change, the necessity of international political responses has emerged. An important step was launched in 1992 at Rio de Janeiro Earth Summit, where 130 nations signed a Convention on Climate Change. The ultimate objective of this convention was the “stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system” [2]. Negotiations in 1995 to strengthen the global response to climate change lead to the Kyoto Protocol, adopted in 1997 and

signed by 192 parties. The latest historical step to combat climate change took place at the Paris climate conference (COP21) in 2015, where 195 countries have set out the first international climate agreement. Governments agreed a long term global action plan to overcome dangerous climate change by limiting global warming to well below 2 °C [3].

According to the above mentioned it is urgent to apply alternative eco-friendly methods to produce energy and limit global greenhouse gases emissions. In this context, non-containing sulfur biofuels, such as bioethanol and biodiesel, have attracted full attention in recently years, considering their lower environmental impact.

The most promising method for biodiesel production is transesterification, reaction between a primary or secondary alcohol and vegetable oils, animal fats or waste cooking oil, in presence of acidic, basic or enzymatic catalysts generating glycerin as a by-product [4,5].

One drawback of the process relies on the immiscibility of the alcohol and the vegetable oil, which engenders mass transfer resistance slowing reaction rate. In this regard, several research studies have aimed at finding optimal mass/heat transfer conditions for biodiesel production to save time and energy. These

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investigations include ultrasound [6], microwave [7], and supercritical conditions [8].

In the other hand, since the reaction rate of biphasic heterogeneous systems depends on the reagents surface area, a vigorous mixing has been suggested to create an emulsion and promote an efficient contact between the two immiscible phases [9]. However, the experiment using high speed mixers in biodiesel manufacture involved high energy consumption due to the reaction temperatures employed [10–15]. For instance, Chen [11] compared various published continuous transesterification reactors concluding that the Rotating Packed Bed reactor was the best due to its excellent micro-mixing characteristics. Qiu [12] reviewed some modern technologies for the transesterification reaction, which use static mixers, and micro-channel reactors oscillatory flow, cavitation, or microwave reactors. In addition, membrane reactors, reactive distillation and centrifugal contactors as novel reaction/separation coupled technologies were analyzed. Nouredini [13] studied the motionless mixers versus a high-shear reactor. The best result using the motionless mixer, at 70 °C, 8:1 M ratio, and 6–8 min was obtained. Da Silva [14] reported the use of a multiple-stage ultra-shear reactor. An ester conversion of 99.3% was achieved from a 6:1 ethanol:soybean oil molar ratio, 1.35 wt % NaOH concentration, 78 °C, and 12 min of reaction time. Choedkiatsakul [15] used a multi-rotor high-shear mixer (Magic-Lab, IKA) connected to a multimode microwave reactor (system 1) and compared with a high-shear mixer (system 2). Both systems, coupled to a recycle pump, spent 1 min for each cycle. A full conversion was achieved in 5 min from system 1 and 91.57% from system 2. However, system 1 required noticeably higher consumption energy (1200 kJ L⁻¹) compared to system 2 (263 kJ L⁻¹) for a 5 cycles period and a 9:1 MeOH/oil ratio.

Even a huge quantity of processes to produce biodiesel have been published, research continues to discover an industrially attractive approach to afford high yield in a very short time and low energy consumption.

In this work, a simplified methodology for biodiesel production at room temperature and ambient pressure by means of a ROSS High-Shear Mixer is reported. The produced nanodroplets deliver an effective contact among reactants, minimizing mass transfer resistance and producing a quantitative conversion of FAME. The effect of dispersion rate and time, vegetable oil:methanol molar ratio, catalyst type and amount were studied. To verify if the process herein presented is applicable to other vegetable oils, four vegetable oils were evaluated. Likewise, an energy consumption comparison using the high shear mixing and a traditional laboratory biodiesel production was carried out.

2. Experimental

2.1. Materials

Refined soybean, corn, canola, olive and sunflower oil were purchased from local suppliers and were used as received without further purification. Vegetable oils acidity values were determined by the ASTM D 974-97 method [16].

NaOH (85%), KOH (99%), H₂SO₄ (98%) and HCl (36.5% purity) were purchased from Golden Bell, Meyer and Sigma-Aldrich. Technical grade MeOH, from Meyer was distilled and dried (using metallic magnesium turnings and iodine) before reactions.

Dispersions were performed using a ROSS HSM-100 LCI high shear mixer, which consists of a single stage rotor that turns at high speed within a stationary stator (a fine screen stator head dispersion attachment was used in all experiments). As the rotating blades (fine rotor) turn around the stator, both mechanically shear the crude mixture.

2.2. Characterization

2.2.1. Proton nuclear magnetic resonance (¹H NMR)

¹H NMR spectra were measured on a Varian Mercury 300 MHz spectrometer, using deuterated chloroform (CDCl₃) as solvent. The residual protonated solvent signal (7.26 ppm) was used as shift reference. The methoxy group signals of FAMES (3.66 ppm, singlet) and the methylene protons of the residual glycerin triesters (4.14–4.27 ppm, two doublet of doublets) were chosen to calculate the transformation ratio. Conversion was calculated from the integrated areas of the aforementioned signals following the procedure described by Knothe [17]. Spectra of crudes at best conditions were analyzed using a Bruker Avance III TM-500 MHz spectrometer to improve the signal/noise ratio to detect any residual signals of mono-, di- or triglycerides. By means of the installed cryogenic probe (at least 16 scans), traces about 0.5% could be detected. NMR experiments permit to assure the quantification of oil conversion to biodiesel.

The effect of the catalyst amount (0.35–1 wt %), dispersion speed (1000–4000 rpm), dispersion time (25–60 s), methanol:oil molar ratio (2–6), and catalyst nature (KOH, NaOH, H₂SO₄ and HCl) were investigated. All experiments for one conditions set were repeated three times (statistical error bars are included in the corresponding figures).

3. Results and discussion

3.1. Effect of the catalyst amount

Initially, 100 mL of MeOH and 400 mL of soybean oil (6:1 MeOH/soybean oil molar ratio) were placed into a jacketed glass vessel to keep the reaction temperature at 25 °C. Then the effect of NaOH as catalyst was examined from 0.35 to 1.0 wt %. Fig. 1 shows the conversion trend as a function of the catalyst amount at a constant dispersion time (60 s) and speed (4000 rpm). An experiment without catalyst was conducted; it permitted to verify that although an emulsion between the vegetable oil and methanol was initially obtained it was unstable and no conversion into biodiesel was detected, revealing that catalyst was essential. In the second run, ~87% conversion was achieved using 0.35 wt % catalyst, while in the third run (0.5% catalyst) 97% conversion was produced. In the

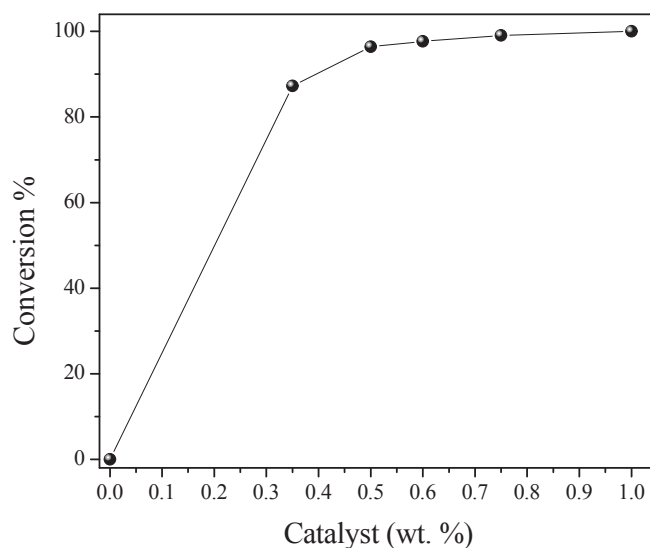


Fig. 1. Effect of the catalyst amount. Dispersion rate, 4000 rpm; dispersion time 60 s; MeOH:vegetable oil ratio, 6:1; reaction temperature, 25 °C.

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