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EXPLORATORY STUDY ON INTERNAL RECYCLING OF CRUDE GLYCEROL FOR BIODIESEL PRODUCTION: CATALYST REPLACEMENT

Article Highlights

- Crude glycerol was recycled as source of catalyst for biodiesel production
- Methanol and catalyst distribution in crude glycerol was affected by their initial concentrations
- Biodiesel with a purity of 99.3 wt.% was obtained under conventional reaction conditions
- Using crude glycerol, higher methanol:oil mole ratio (12:1) was required for biodiesel synthesis
- Biodiesel with a purity of 96.9 wt.% was obtained by recycling crude glycerol

Abstract

The present study evaluated the recycling of crude glycerol as source of catalyst for biodiesel production. For that purpose, two sets of experiments were conducted. In the first set A, biodiesel was synthesized by conventional methanolysis of sunflower oil using NaOH as catalyst at 65 °C during 1 h and varying catalyst concentration (0.4-1.2 wt.%) or methanol to oil mole ratio (6:1--12:1). The second set (B) was performed by replicating the conditions of set A and considering the use of crude glycerol as source of catalyst. The evaluation of excess methanol and catalyst distribution in the crude products was performed. For both sets of experiments, product yield and quality (viscosity and purity) were determined. Methanol was predominantly in the glycerol phase (54-68%), with negligible effect of variation in catalyst concentration and higher percentages found when higher methanol to oil mole ratios were used, due to a higher polarity of this phase. In most cases, catalyst was predominantly in the crude glycerol (53 wt.% in average) and no clear relation was found between catalyst distribution and the different reaction conditions studied. The results from set A showed a clear influence of catalyst concentration in biodiesel conversion and a minor effect of methanol to oil molar ratio. The best conditions were 6:1 methanol to oil mole ratio and 0.6 wt.% of catalyst leading to a product yield of 95.1 wt.%, a purity of 99.3% and a viscosity of 4.59 $mm^2 s^{-1}$*. The second set of experiments, B, showed different trends and variability compared to the first one, and the results indicated that catalyst might be altered during glycerol storage. It was found that the methanol to oil mole ratio affected the reaction conversion, with the highest purity (96.9 wt.%) being obtained when the highest mole ratio was used (12:1), possibly due to the reduced mass transfer limitations. Overall, the results clearly show the potential of using crude glycerol as source of catalyst, avoiding the use of new catalyst and allowing a more sustainable biodiesel production.*

Keywords: crude glycerol recycling, glycerol composition, catalyst recycling, methanolysis.

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Biofuels, particularly biodiesel and bioethanol, are accepted as environment-friendly automotive fuels that contribute for the establishment of a diverse and sustainable net of energy sources to respond to the current high energy demand and, at the same time, reduce as much as possible the use of fossil resources and related impacts.

Biodiesel is the most produced biofuel in Europe; its synthesis is conventionally performed using an alkali-catalysed transesterification reaction, which converts different triglyceride sources, mostly refined vegetable oils, into biodiesel – mono alkyl esters (t/t_{oil} around 1) and the by-product glycerol (around 0.1t/t_{oil}) [1,2].

Independently from the raw materials, which have the most significant weight in the production costs and led to a wide range of studied alternatives [3], the economic viability of biodiesel production is also dependent upon the glycerol value. However, currently, with the increasing production of biodiesel, the glycerol market has become saturated, with significant economic impacts for the biodiesel and synthetic glycerol production companies [4]. In agreement, a wide range of studies can be found concerning glycerol reuse and recycling namely for the production of chemicals, fuel and fuel additives, co-digestion, co-gasification and co-pyrolysis, fuel cells and wastewater treatment [4,5].

Taking into account the current status, the exploitation of glycerol reuse within the biodiesel production process should be considered a priority, not as a way to use all the by-product, which might be also converted into additional value-added products, mostly by other industries, but as a way of taking advantage from its potential to reduce production costs and use it internally as a value-added product. From the studied processes, the following are highlighted: free fatty acid esterification by crude glycerol, as an alternative to lower the free fatty acid content of waste raw materials [6] and, heterogeneous catalyst production for use during esterification and transesterification processes [7,8].

When considering the methanolysis (most used route) and using conventional reaction conditions (6:1 methanol to oil mole ratio and 1 wt.% alkali catalyst), the distribution of the remaining reactants shows that most of the alcohol and catalyst is present in the glycerol-rich phase, rather than in the ester-rich phase. Most of the studies on glycerol characterization, also used as reference in more recent related manuscripts [9], refer to the year 2006. Zhou and Boocock [10] showed that, under conventional reaction conditions, and using soybean oil as raw material, the crude glycerol (before alcohol recovery) was composed by 60% of glycerol, 33% of alcohol, less than 1% of ester and 5.57% of sodium methoxide catalyst, which corresponded to 58% of the alcohol and 94.2% of the catalyst used in the biodiesel production. In a study by Kocsisová and Cvengroš [11], the crude glycerol composition is stated as variable, depending in particular of the acid value of the raw material. The following general composition is presented: 50-60% glycerol, 12-16% of alkalis (soaps and hydroxides), 15-18% of methyl esters, 8-12% methanol and 2-3% of water. In a study by Thompson and He [12], the characterization of crude glycerol from transesterification under standard conditions (using sodium methoxide) and with different raw materials (ex. rapeseed, soybean, crambe and waste vegetable oils) showed variable results, the waste source having the highest variation, due to the poor conversion obtained under similar conditions, which led to a significant presence of unreacted glycerides (measured as fat content) compared to other raw materials as well as higher ash content (mainly sodium from the catalyst). Considering all raw materials, the ash content varied from 0.7 to 5.5 %.

Taking into account the mentioned studies, there is no doubt that a great amount of catalyst remains in the crude glycerol by-product and, in agreement, the objective of the present study was to evaluate the internal recycling of glycerol as source of catalyst. For that purpose, two sets of experiments were conducted. In the first set A, biodiesel was produced using refined soybean oil and NaOH as catalyst; and, in the second one, B, the experimental conditions were replicated, but, instead, the crude glycerol was used as source of catalyst. The effect of different reaction conditions on the product yield and quality were evaluated by varying catalyst concentration and methanol to oil mole ratio whereas the temperature and the reaction time were kept constant (65 °C, 1 h).

MATERIALS AND METHODS

Materials

Sunflower oil was commercial oil from the brand "*3Ás Equilíbrio*", being donated by Sovena, SA, Portugal and used without further treatments. Methanol 99.8% (VWR, AnalaR Normapur) and NaOH ≥ 98% (Sigma-Aldrich, pellets) were used for biodiesel synthesis. HCl solutions (determination of catalyst concentration and acid washing) were prepared using HCl by Merck (analytical grade).

For validation of the analytical method for catalyst determination in glycerol, commercial glycerol of the brand Higilim was used.

Methods

Biodiesel synthesis

Biodiesel was produced in a round bottom 500 mL glass flask, immersed in a thermostatic bath and equipped with a water cooled condenser and magnetic stirring. The oil was initially charged to the reactor and stabilized at the desired temperature after which the methoxide solution prepared (methanol and catalyst in defined amounts) was added and vigorous magnetic stirring was promoted. The reaction progressed during the defined period. Experimental conditions were defined according to an experimental planning, further described.

Biodiesel purification was performed by excess methanol removal (rotary evaporator) and acid/water washing [1]. Biodiesel drying was made by heating in a heating plate (slightly higher temperature than 100 °C) under constant magnetic stirring. Heating method was validated by Karl Fisher water measurements which shown a water content of the product always bellow 500 mg kg^{-1}. Crude glycerol was also subjected to methanol removal in the rotary evaporator [1]. In this case, the weight difference was registered to quantify methanol present. The crude glycerol was kept at 4 °C until reuse.

Experimental planning

The experimental planning was conducted in order to evaluate the influence of the catalyst concentration as well as the methanol to oil molar ratio on product purity and viscosity, and to compare the traditional process with that resulting from reusing glycerol.

Two sets of experiments were conducted: A and B. In the experiments A, NaOH was used as catalyst whereas in the experiments B the glycerol obtained from set A was used as a source of catalyst (as after detailed). The range of catalyst concentration varied from 0.4–1.2 wt.%, in agreement with Dias *et al.* [1]; the methanol to oil molae ratio varied from 6:1 to 12:1 to evaluate the effect of the changing the traditional ratio (6:1) [1] to a larger excess (which could affect the reagents distribution between glycerol and biodiesel phases).

The reference conditions considered were: 0.6 wt.% of catalyst and 6:1 methanol to oil mole ratio. When varying the catalyst concentration, the methanol to oil molar ratio was kept under the reference value and when the variation of methanol to oil molar ratio was studied the catalyst concentration was maintained in the reference value.

For all experiments, the temperature was set as 65 °C and the reaction time was 1 h.

For set A, the mass of oil used was always 200.0 g; for set B, the glycerol mass was fixed at 15 g (to ensure that enough mass existed for all the conitions) and the amount of oil and methanol was added taking into account the catalyst concentration in the glycerol phase, to ensure the same reaction conditions. All the experiments were carried out in duplicate.

A total of 24 experiments were performed and the reaction conditions used for both sets are presented in Table 1.

Table 1. Experimental planning

Experiment (A/B)	Catalyst concentration wt.%	Methanol:oil mole ratio
1A/1B	0.6	6:1
2A/2B	0.6	12:1
3A/3B	0.8	6:1
4A/4B	0.6	9:1
5A/5B	0.4	6:1
6A/6B	0.6	6:1
7A/7B	0.8	6:1
8A/8B	1.2	6:1
9A/9B	0.6	12:1
10A/10B	1.2	6:1
11A/11B	0.6	9:1
12A/12B	0.4	6:1

Determination of catalyst concentration in glycerol

The determination of catalyst concentration in glycerol was performed by volumetric titration, using a standardized solution of HCl (0.1 M), phenoftalein as indicator and water as solvent. To validate the method, 0.42 g of NaOH were dissolved in 6.00 g of commercial glycerol (three replicates were performed) and after the mentioned procedure was applied.

Determination of biodiesel quality

Taking into account the objective of the present study, which was to preliminary evaluate the viability of internal glycerol recycling, two key quality parameters were evaluated, in agreement with the study by Dias *et al.* [1]: methyl ester content and viscosity. The kinematic viscosity was determined at 40 °C using glass capillary viscometers, according to the standard ISO 3104 (1994), and the methyl ester content was determined by GC, according to the standard EN 14103 (2003). To validate the dehydration method, the water content was determined by Karl Fischer coulometric titration, according to the standard NP EN ISO 12937 (2003).

In addition to the quality parameters, biodiesel yield (100×mass of product/mass of oil) was also determined.

RESULTS AND DISCUSSION

Distribution of excess methanol and catalyst in crude biodiesel and glycerol

The results of the validation of the titrimetric method for determination of the amount of catalyst in glycerol showed that the method was accurate, since the difference between the theoretical and the experimental values was less than 1%.

As it was considered relevant to evaluate the distribution of the excess methanol and catalyst between the crude glycerol and biodiesel, their quantification was made for crude glycerol obtained in Set A (amount in biodiesel was determined as the difference to 100%). Results are presented in Figure 1.

It is clear that the variation in catalyst concentration does not affect how excess methanol is distributed in both phases. The results showed that under standard conditions (6:1 methanol to oil mole ratio) the excess methanol is mostly present in the glycerol phase, although differences are not very high, being in average close to 55% of total. The results completely agree with those obtained by Thompson and He [12] (54% of methanol in the glycerol phase). When the methanol to oil molar ratio increased it led to an increase of the amount of alcohol in the glycerol phase, with results varying in average from 54 to 68%. This fact should be due to the increase of the polarity of the glycerol phase with increasing methanol concentration. This is the opposite of what is observed when using ethanol, which is less polar and tends to be more easily dissolved in the ester phase than methanol, thus increasing the ester phase polarity and therefore increasing the amount of alcohol in this phase, as observed by Zou and Boocock [10].

The results regarding the catalyst percentage in the crude glycerol, as function of catalyst concentration and variation of methanol to oil mole ratio are presented in Figure 2.

In what relates catalyst concentration, and compared to the experimental set A, results for Set B showed a higher degree of variation of catalyst distribution as function of catalyst concentration as well as a higher variation between experiments. The results varied from 32 to 66 wt.% of catalyst in the glycerol phase, in average, and were low in comparison to what is stated in the literature, which reports more than 90% [10]. In what relates the methanol to oil molar ratio influence, the variation was not very expressive despite a clear trend indicate that at lower mole ratios (6:1 and 9:1) the catalyst is more predominantly in the glycerol phase (around 60%) whereas at the higher mole ratio (12:1) it is more equally distributed in both phases. Taking into account the increase of polarity by increasing methanol concentration in glycerol, it would be expected that an increase of methanol to oil molar ration would lead to an increase in catalyst concentration in this phase which would more easily dissolve the catalyst [10]. The results obtained for both parameters might be related to variation in the form of the catalyst present in the glycerol which could affect catalyst distribution between both products at the different con-

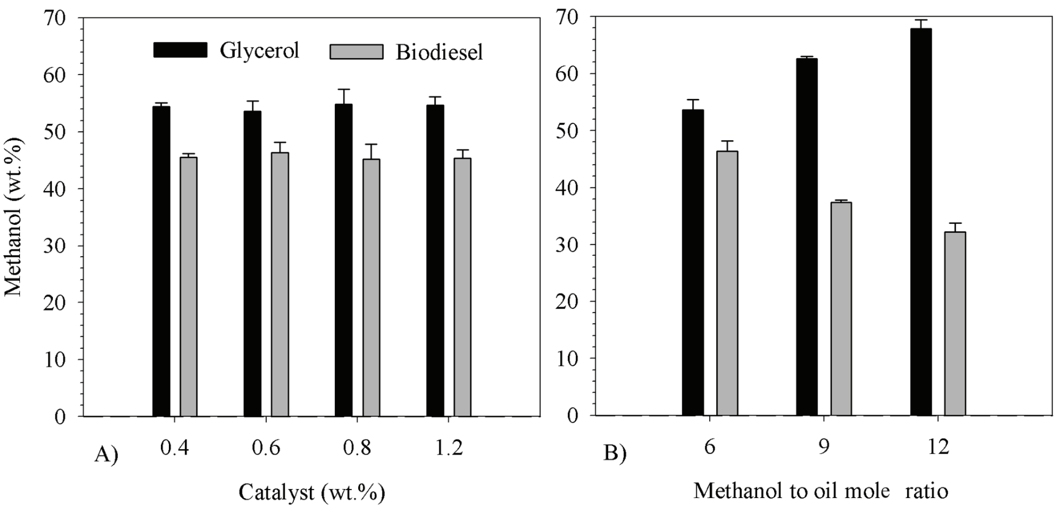

Figure 1. Distribution of excess methanol in the crude biodiesel and glycerol phases: Influence of catalyst concentration (A) and methanol to oil molar ration (B).

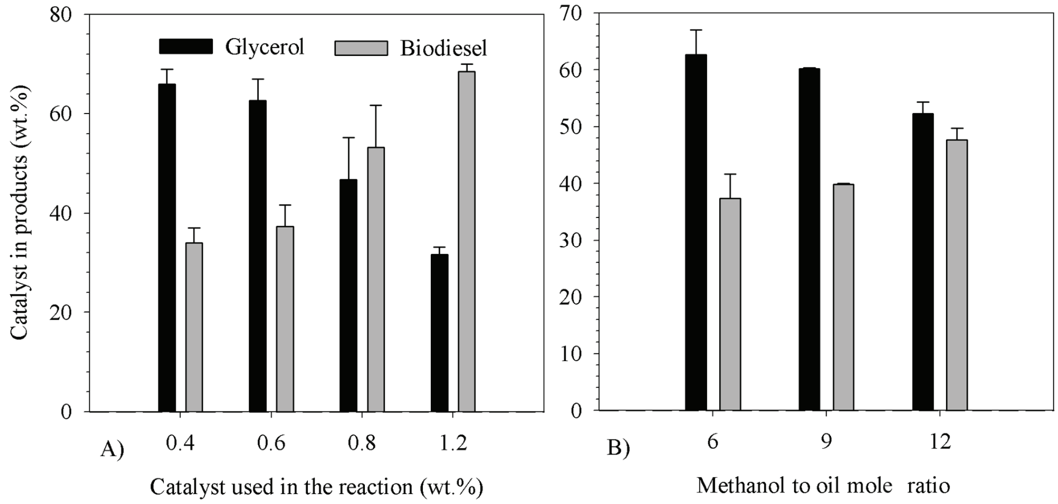

Figure 2. Amount (wt.%) of catalyst in crude glycerol as function of catalyst concentration (A) and methanol to oil molar ratio (B).

ditions studied. It should be emphasized that in the present study soaps were not determined, taking into account the information presented by Zhou and Boocok [10] and reinforced by Chiu *et al.* [13], that the soap production was not expected to affect phase distribution.

Product yield

Figure 3 shows the results regarding the product yield using different catalyst concentrations and methanol:oil mole ratios, taking into account both sets of experiments. The results varied in average from 82.7 to 95.6 wt.%.

The results of set A of experiments show very small degree of variation within replicates whereas in set B overall yields were slightly lower and the results showed a higher variation among experiments.

In terms of the different studied variables, for both sets of experiments, a clear influence of the catalyst concentration on product yield exists, whereas the variation of methanol:oil mole ratio presented negligible effect, as reported by Leung and Guo [14]. The catalyst concentration effect was especially evident when catalyst concentration increased to values higher than 0.6 wt.%. This fact could be attributed to higher difficulties during product purification (washing) at higher catalyst concentration, which causes product loss and therefore a decrease in product yield as previously observed [1].

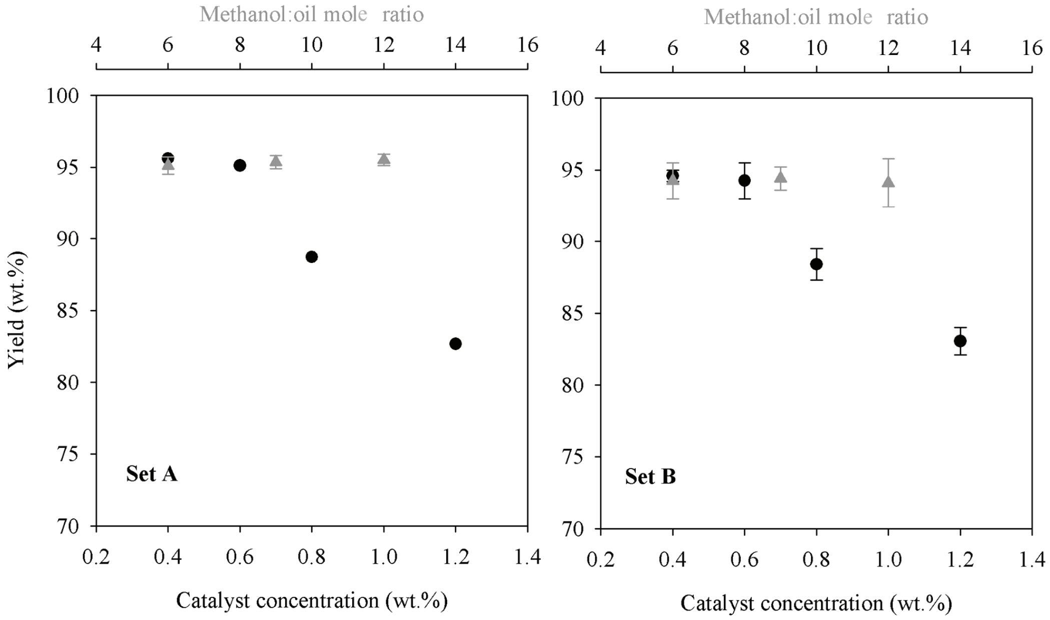

Figure 3. Influence of catalyst concentration and methanol:oil molar ratio in product yield for set A and B of experiments.

Product quality

The set A results regarding the product viscosity and purity using different catalyst concentrations and methanol:oil mole ratios are presented in Figure 4.

In terms of viscosity, it is possible to observe that as the catalyst concentration increases, there is a slight reduction of the product viscosity (Figure 4A). Such results indicate higher conversions at higher catalyst concentrations, fact validated by Figure 4B, which shows a higher product purity under such conditions. The results completely agree with those reported by Dias *et al.* [1]. In terms of methanol to oil mole ratio, the results presented in average a small variation, being in agreement with the results found by Moreira *et al.* [15] when using poultry fat as raw material. Because in the case of catalyst concentration, the purity result was close to the standard (97.2 wt.%), the use of 0.6 wt.% would be considered the best condition, which allowed obtaining a purity of 99.3 wt.% and a viscosity of 4.59 mm^2 s^{-1}.

The results for the Set B of experiments show a high variability of the results between replicates, especially at 0.8 wt.% catalyst concentration and when a 12:1 methanol to oil mole ratio was used (Figure 5).

Under such conditions, and in the case of the samples with high viscosity (full in the graph), the viscosity results are close to those of the original oil, which shows that the conversion was residual. This fact is confirmed by the purity results obtained for the same samples (Figure 5B). Note that, as expected, an inverse linear correlation exists between purity and viscosity results ($r^2 = 0.9738$, $p < 0.001$ using an F test).

The results seem to indicate that catalyst suffered changes. It was hypothesized that the variations found could be related to catalyst deterioration during storing. As mentioned in 2.2.1, catalyst was kept at 4 °C. However, the storage period was different between experiments, as such effect was not anticipated. By evaluating the time of storage, it was verified that for the same reaction conditions, the glycerol with higher storage time led to a biodiesel product with higher viscosity and lower purity, indicating catalyst deterioration. The following factors could have occurred: *i*) increase of water content of glycerol, which increases glycerol mass and alters catalyst concentration; and, *ii*) production of Na_2CO_3 (inactive as catalyst) by contact of glycerol with air. Taking into account the variations observed, the influence of catalyst concentration in both viscosity and purity cannot be inferred, although between 0.4 and 0.8 wt.% (excluding the unexpected result at 0.8 wt.%), the trends appear to be similar to those obtained in Set A of experiments.

If we consider that the result of high viscosity at 12:1 methanol to oil mole ratio is an outlier, it seems that the viscosity, and consequently purity, are affected by methanol concentration, with lower viscosities and higher purities being found at higher methanol amounts. So, in the case of Set B, contrary to what occurs in Set A, methanol to oil mole ratio affects reaction conversion. This might be due to the fact that when methanol amount increases it facilitates the contact between reactants and catalyst

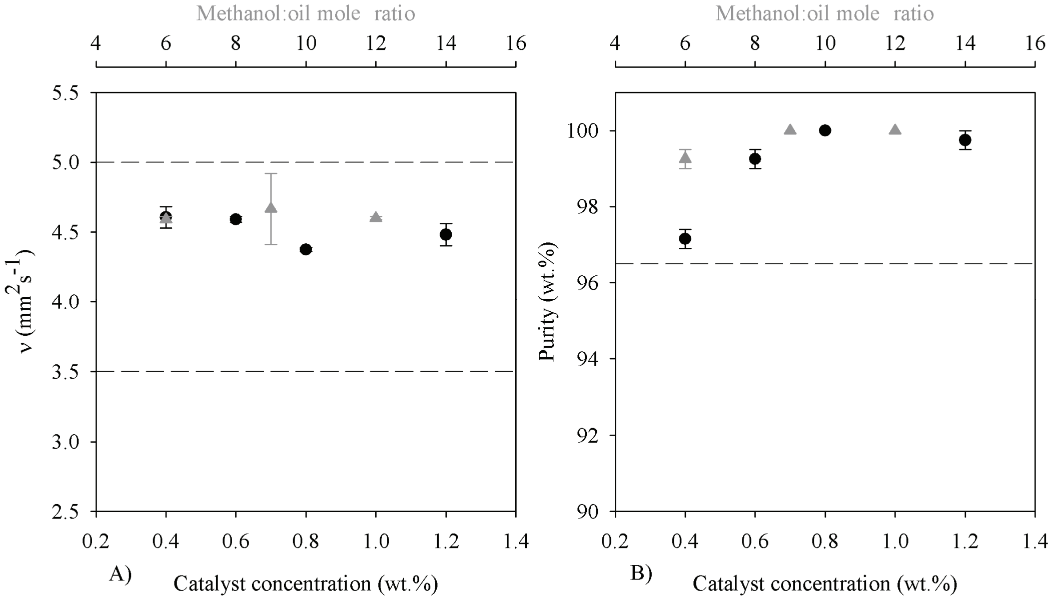

Figure 4. Influence of catalyst concentration and methanol:oil molar ratio in biodiesel viscosity (A) and purity (B), for Set A of experiments.

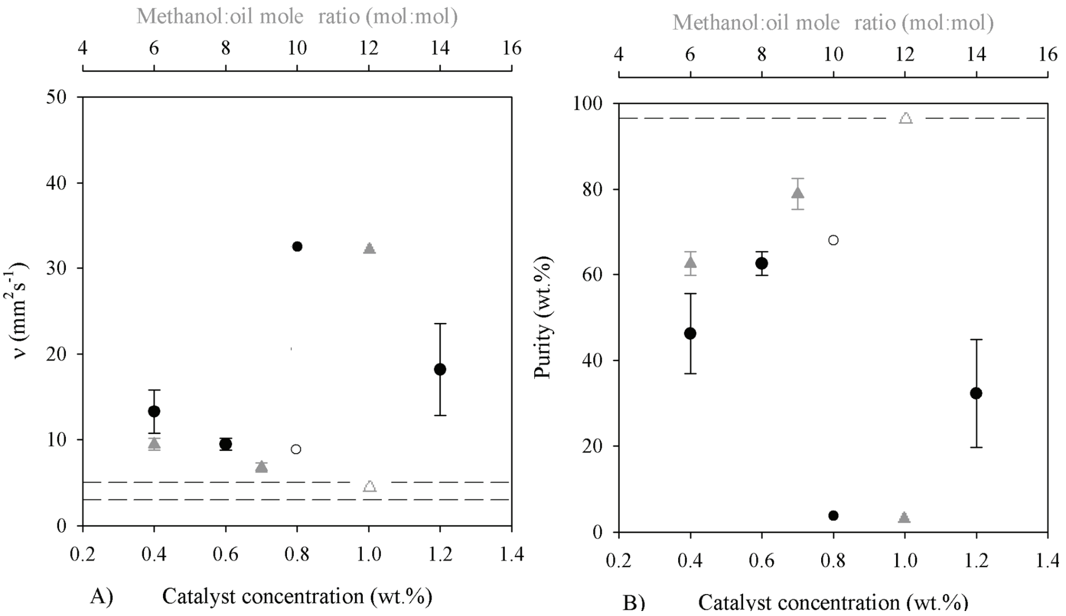

Figure 5. Influence of catalyst concentration and methanol:oil mole ratio in biodiesel viscosity (A) and purity (B), for Set B of experiments. For results at 0.8 wt.% catalyst and 12:1 methanol to oil mole ratio the results of each replicate are presented due to differences found.

present in crude glycerol (glycerol is more diluted), reducing mass transfer difficulties and therefore leading to higher conversions. This is different than what occurs in the experiments from Set A.

Validation

Taking into account the variations found in results from Set B of experiments, an additional experiment was conducted, aiming to validate results obtained in experiment 9B (higher purity and lower viscosity at 12:1 methanol to oil mole ratio and 0.6 wt.% of catalyst). In this case a glycerol obtained from applying such reaction conditions was used. The following results were obtained: product yield of 96.8 wt.%, viscosity of 5.01 mm^2 s^{-1}, and, purity of 95.1 wt.%. Although some differences might be observed, there is no doubt that the results are within the same order of magnitude from those obtained previously under such conditions.

The results from this preliminary assessment show that it is possible to perform an internal recycling of crude glycerol aiming catalyst replacement and obtain a high purity of the final product. Additional studies on optimization should take into account mass transfer limitations between the oil /crude glycerol phases under different reaction conditions and catalyst alteration during storage.

CONCLUSION

Two sets of experiments were conducted aimed first at conventionally producing biodiesel and glycerol using NaOH catalyzed methanolysis and after using the crude glycerol from the first set of experiments as source of NaOH to replicate the study in a second set of experiments.

Taking into account their potential influence in crude glycerol composition, the variation of catalyst concentration (0.4-1.2 wt.%) and methanol to oil mole ratio (6:1-12:1) was evaluated during biodiesel synthesis.

Both methanol and catalyst were predominantly found in the crude glycerol phase with higher expression of methanol in glycerol, compared to biodiesel, when higher methanol to oil mole ratios were used, due to higher polarity of the glycerol phase.

In general, the yields did not present a high degree of variation (90–96 wt.%) except when the highest catalyst concentration studied was employed, where lower values were obtained (around 80%).

The first set of experiments showed a high product quality in all conditions studied, with a clear influence of catalyst concentration and residual influence of methanol to oil mole ratio towards reaction conversion. Best conditions were established as 0.6 wt.% catalyst and 6:1 methanol to oil mole ratio, leading to a product with a purity of 99.3 wt.%.

The second set of experiments showed overall worse results in comparison to set A and the variations observed indicate that catalyst might be altered during storage. In this case, a clear positive effect of increasing methanol to oil molar ratio in product conversion was found possibly due to reduced mass transfer limitations and it was possible to obtain a product with high purity (96.9 wt.%) using a methanol to oil mole ratio of 12:1 and a catalyst concentration of 0.6 wt.%.

The present study confirms the potential of performing internal recycling of crude glycerol as source of catalyst for biodiesel production, avoiding the use of new catalyst with the associated benefits for a more economic and environment-friendly process.

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NAUČNI RAD

PROUČAVANJE MOGUĆNOSTI RECIKLISANJA SIROVOG GLICEROLA U PROIZVODNJI BIODIZELA: ZAMENA KATALIZATORA

Ova studija procenjuje reciklisanje sirovog glicerola kao izvor katalizatora za proizvodnju biodizela. U tu svrhu, sprovedena su dva seta eksperimenata. U prvom setu (A), biodizel je sintetisan konvencionalnom metanolizom suncokretovog ulja korišćenjem NaOH kao katalizator na 65 °C tokom 1 h i različitim koncentracijama katalizatora (0,4-1,2%) i molskog odnosa metanol/ulje (6:1-12:1). Drugi set (B) je izveden pod uslovima seta A i razmatra upotrebu sirovog glicerola kao izvora katalizatora. Izvršena je procena viška metanola i raspodele katalizatora u sirovim proizvodima. Za oba seta eksperimenata, određeni su prinos i kvalitet proizvoda (viskoznost i čistoća). Metanol je bio uglavnom u glicerolnoj fazi (54-68%), sa zanemarljivim uticajem variranja koncentracije katalizatora i većim procentima pri većem molskom odnosu metanol/ulje, zbog veće polarnosti ove faze. U većini slučajeva, katalizator je pretežno u sirovom glicerola (53% u proseku) i nije pronađen jasan odnos između distribucije katalizatora i različitih reakcionih uslova. Rezultati iz seta A pokazuju jasnu uticaj koncentracije katalizatora na konverziju i manji efekat molskog odnosa metanol/ulje. Najbolji uslovi su molski odnos metanol/ulje 6:1 i količina katalizatora 0,6%, koji vode prinosu proizvoda od 95,1%, čistoće od 99,3% i viskozitetu 4,59 mm^2 s^{-1}. Drugi set eksperimenata je pokazao različite trendove i varijabilnost u odnosu na prvi, a rezultati su ukazali da se katalizator može menjati tokom skladištenja glicerola. Utvrđeno je da je molski odnos metanol/ulje uticao na konverziju, pri čemu je najveća čistoća (96,9%) dobijena kada je korišćen najveći molski odnos (12:1), verovatno zbog smanjenih masenoprenosnih ograničenja. Sve u svemu, rezultati jasno pokazuju potencijal korišćenja sirovog glicerola kao izvora katalizatora, čime se izbegava upotreba novog katalizatora i omogućuje više održiva proizvodnja biodizela.

Ključne reči: reciklisanje sirovog glicerola, sastav glicerola, reciklisanje katalizatora, metanoliza.