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Abstract

The performance of oil, gas and gas condensate wells is determined by the qualitative condition of the bottomhole zone of a rock, which is mainly characterized by its permeability, that is, the ability to filter the wells for extraction of hydrocarbons. This characteristic of the rock tends to deteriorate from the moment of first opening of the rock, and continues to deteriorate during the operation of the well. Nowadays, to increase the permeability of oil-and-gas rocks, various methods of physical and chemical effects are widely used. The article is dedicated to a new direction of increase of the permeability of oil-and gas rocks, based on their treatment by atomic and molecular hydrogen.

The results of experimental studies were presented. They proved that hydrogen is an activator of the diffusion processes in the oil-and-gas bearing rocks, and it increases their permeability. Moreover, the maximum increase of the permeability of cores was reached by the effect of the atomic and molecular hydrogen, produced in a reactor by hydrolysis of hydroreacting substances directly during the processing.

The results of the studies offer the perspectives for application of hydrogen technologies for intensification of oil, gas and gas condensate extraction.

Keywords: *hydrogen permeability, core, diffusion, well, activation*

Для виробництва біодизелю доцільно проводити реакцію переетерифікації із використанням гетерогенного каталізатору. Досліджувались три каталізатори: MgO, CaO, $NaAlO_2$. Встановлено залежність виходу бутилових ефірів від кількості каталізатору, часу реакції та надлишку спирту

Ключові слова: бутилові ефіри, каталізатор гетерогенний, переетерифікація, олія соняшникова

Для производства биодизеля целесообразно проводить реакцию переэтерификации с использованием гетерогенного катализатора. Исследовались три катализатора: MgO, CaO, $NaAlO_2$. Установлена зависимость выхода бутиловых эфиров от количества катализатора, времени реакции и избытка спирта

Ключевые слова: бутиловые эфиры, катализатор гетерогенный, переэтерификация, масло подсолнечное

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OPTIMIZATION PROCESS OF BIODIESEL SYNTHESIS USING HETEROGENEOUS BASE CATALYSTS

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1. Introduction

Biodiesel is an alternative fuel for diesel engines that is gaining attention in the Ukraine after reaching a considerable level of success in European Union countries and United States. Its primary advantages are that it is one of the most renewable fuels currently available and it is also non-toxic and biodegradable. It can also be used directly in most diesel engines without requiring extensive engine modifications [1]. Thus it provides a feasible solution to

the twin crises of fossil fuel depletion and environmental degradation. Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety [2].

Base catalyzed transesterification is the most economical process used to production the biodiesel [3]. Base-catalyzed transesterification involves stripping the glycerin from the fatty acids with a catalyst such as sodium or potassium hydroxide, and replacing it with an anhydrous alcohol. The resulting raw product is then centrifuged and washed with water to cleanse it of impurities. This yields fatty acid ester (biodiesel), as well as a smaller amount of glycerol, a valuable by-product used in making soaps and numerous other products [1]. An alternative method for the production of biodiesel is to use heterogeneous solid catalysts in the transesterification process. Heterogeneous solid catalysts have the general advantage of easy separation from the reaction medium and reusability. Heterogeneous catalysis is thus considered to be environmental process. The process requires neither catalyst recovery nor aqueous treatment steps: the purification steps of products are then much more simplified and very high yields of fatty acid esters, close to the theoretical value, are obtained [4].

However, the disadvantages of heterogeneous catalysts are their deactivation with time owing to many possible phenomena, such as poisoning, coking, sintering, and leaching [5]. In general, the best heterogeneous base catalysts must have several qualities i.e., catalyze transesterification and esterification, not be deactivated by water, be stable, do not give rise to leaching, be active at low temperature, and have high selectivity [6]. Thus, the use of heterogeneous base catalysts to produce biodiesel requires a better understanding of the factors that govern their reactivity, such as operating conditions (catalyst concentration, reaction temperatures, and reaction time). This paper provides an experiment three different heterogeneous base catalysis for biodiesel production with environmental benignity, transesterification of edible sunflower oil with butanol.

2. Materials

Sunflower oil with acid value of 1.8±0.04mgKOH/g and butanol were used in this research as the feedstock while Magnesium oxide, Calcium oxide, Sodium aluminate were used as catalysts.

3. Experiments

The set of experiments conducted to investigate the effects of four factors; catalyst type, catalyst concentration, reaction time, and butanol to oil molar ratio on the conversion of oil into butyl ester. The catalyst concentration was compared on weight percent. The reactions were carried out a 500ml round bottom one neck flask and a water–cooled condenser that returned any vaporized butanol to the reacting mixture. The reaction temperature was ~150°C using a hot plate magnetic stirrer.

Sunflower oil (100 g) and the desired butanol and catalyst amount were transferred into the flasks and placed in the hot plate magnetic stirrer. All experiments were run in triplicate. After 60 min agitation the reacted mixtures were transferred to separator funnels and the glycerol was separated after settling. The butanol was then removed from both butyl ester and glycerol layer by heating at 118°C for 30 min.

The experiments were compared based on two process parameters: yield and the total glycerin content of butyl ester. The content of total glycerin was monitored by using official test method Ca 14–56 (AOCS, 1991) for total, free, and combined glycerol (iodometric–periodic acid method). In official methods and recommended practices of the American oil chemists' society.

4. Results Anddiscussion

The preliminary analysis showed in table the results of investigation the effects of four factors; different heterogeneous base catalysts (*Magnesium oxide*, *Calcium oxide*, *Sodium aluminate),* catalyst amounts (0.5, 1, and 1.5 Wt %.), three reaction time (60, 90, 120 min), and 9:1 molar ratio of butanol to oil, on the yield and total glycerin content of butyl ester.

Table 1

The effects of process evaluation parameters and experimental results on the yield and total glycerin content of butyl ester.

Catalyst type	Run №	Catalyst amount Wt%.	Reaction time (min)	Yield (%)	Total glycerin (%)
MgO	1	0.5	120	57.5	0.63
	2	1.0	90	70	0.37
	3	1.5	60	81.5	0.24
CaO	1	0.5	120	64	0.55
	2	1.0	90	73	0.32
	3	1.5	60	86	0.22
$NaAlO_2$	1	0.5	120	68.5	0.47
	2	1.0	90	80	0.25
	3	1.5	60	89.5	0.20

** For a 9:1 molar ratio of butanol to oil.*

The influence of the catalyst amount on yield of butyl ester is shown in table 1 for a 9:1 molar ratio of butanol to TG at 150 °C. As can be seen, with 0.5 Wt% catalyst of MgO the yield was 57.5 % and the content of total glycerol was 0.63% in 120 min time reaction test, this total glycerin amount was too high to meet the total glycerin specification. However, with 1.0 Wt% of MgO there was a very rapid reduction on the total glycerin to be 0.37% and the yield of butyl ester increased to 70% but still the total glycerin too high. However, increasing the MgO concentration is very effective in decreasing the total glycerin content of butyl ester. When 1.5 Wt% MgO showed a good result, the yield of butyl ester increased to 81.5% and the total glycerin content reduced to 0.24% in 60 min, thus the influence of catalyst will be easier to reduce of time reaction. When excess the feed catalyst concentration more than 1.5 Wt% had a negative effect on reaction yields because it resulted in higher soap formation.

With regard to the second heterogeneous catalyst CaO when 0.5 Wt% in 120 min had used the yield of butyl ester was measured to be 64% with 0.55% total glycerin, when 1Wt% CaO has been used the yield of butyl ester increased to 73% and the content of total glycerin with time reaction

have been reduced to 0.32% in 120min. While the best result was recorded in 60 min with 1.5 Wt% CaO to be 86% butyel ester, 0.22% content of total glycerin. However, after studying the third catalyst NaAlO2 to obtain butyl ester with high quality have been founded by same conditions with 1.5 Wt% in 60 min at 150 °C the yield increased to be 89.5% and the total glycerin content reduced to be 0.20%. In a previous study [7] has indicated that increasing the feed molar ratio between alcohols to feedstocks had a positive effect on reaction yields because it increased the reactant concentration that helps drive the reaction equilibrium forward. And has prompted us to investigate the effect of increasing butanol to oil molar ratio on the yield and total glycerin content of butyl esterto be 12:1, the results were as follows in Table 2.

Table 2

The effects of process evaluation parameters and experimental results on the yield and total glycerin content of butyl ester.

Catalyst type	Run №	Catalyst amount Wt%.	Reaction time (min)	Yield (%)	Total glycerin (%)
MgO	1	0.5	120	58	0.61
	2	1.0	90	72	0.33
	3	1.5	60	83	0.23
CaO	1	0.5	120	66.5	0.50
	2	1.0	90	75	0.35
	3	1.5	60	88.5	0.21
$NaAlO_2$	1	0.5	120	70.5	0.37
	2	1.0	90	85.5	0.22
	3	1.5	60	95	0.18

** For a 12:1 molar ratio of butanol to oil.*

Under the same conditions of the preliminary analysis which were examined are shown in table 1(different heterogeneous base catalysts (Magnesium oxide, Calcium oxide, Sodium aluminate), catalyst amounts (0.5, 1, and 1.5 Wt %.), three reaction time (60, 90, 120 min). Results showed that there were significant differences in product yields among the three catalyst formulations.1.5wt % sodium aluminate gave better yields 95% with 0.18% total glycerin than the 1.5wt % magnesium oxide 83% butyl ester with 0.23 content of total glycerin resulted in higher soap formation in 60 min of time reaction, In spite of good results with used 1.5wt % calcium oxide catalyst which has been investigated 88.5% yield of butyl ester and 0.21% total glycerin but this type of catalyst need more severe operating conditions due to the rapid deactivation by water, which correspond with previous study for synthesis the biodiesel via metal oxide catalyst[5].

5. Conclusions

From the comparison at different concentrations, reaction time, and molar ratios, sodium aluminate catalyst formulations gave better yields than the magnesium oxide; calcium oxide. Solid metal oxides catalysts formulations resulted in higher soap formation than the corresponding sodium aluminate catalyst formulations. The optimum set of process variables was determined by maximizing product yield and minimizing soap formation. The optimized set of conditions was: $NaAlO_2$ as the catalyst at a concentration of 1.5wt%., reaction temperature of 150°C, and a 12:1 molar ratio. Process optimization predicted an optimum yield of 95% with a total glycerin 0.18%.

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Abstract

The most properly used study for biodiesel preparation is via homogeneous transesterification of vegetable oil using alkaline catalysts. Biodiesel yield and oil conversions are affected by a lot of parameters including the catalyst type and amount. The heterogeneous catalysis for biodiesel production has been extensively investigated for the latest few years. This study has evaluated the heterogeneous base catalyst effects on biodiesel yield and total glycerin in transesterification butanol and sunflower oil at different catalyst amount, reaction time and butanol to oil molar ratios. There exist three different heterogeneous base catalysts, magnesium oxide, calcium oxide, sodium aluminate. It has been observed that the sodium aluminate catalyst leads to better butyl ester yields that comply the specification of standard methods (ASTM D 6751 & EN 14214). The highest approximately 95% butyl ester yield acquires 12:1butanol-to-oil molar ratios, 1.5 Wt.% sodium aluminate catalyst at 150°C reaction temperature and 1200 rpm stirring speed under optimum conditions

Keywords: *butyl ester, heterogeneous catalyst, transesterification, sunflower oil*