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Synthesis of biodiesel based on alcohol mixtures

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Abstract

Today, the rapid depletion of traditional fuel sources and rapid global climate change in the environment have increased interest in alternative fuels. The current situation forces many countries to implement different strategies for the development of renewable energy sources. Therefore, the environmental safety of fuels is one of the key factors in ensuring the proper operation of internal combustion engines. These strategies include the synthesis of biodiesel as renewable energy, a promising fuel for diesel engines. The goal of the work was the synthesis of biodiesel fuel from cottonseed oil using a transesterification reaction in the presence of a mixture of small molecular weight alcohols, such as methanol, ethanol, n-propanol and i-propanol, in the presence of H_2SO_4 as a catalyst. The reaction time was 8 hours and the mixture of alcohols was: methanol (ethanol) (34%), propanol-1 (33%) and propanol-2 (33%), yielding 80 and 83%, respectively. From the ^1H NMR spectra, the participation rates of alcohols in transesterification reactions were calculated. The exploitation properties (viscosity, density, ignition temperature, etc.) of the obtained biodiesels are presented according to ASTM standards.

Keywords**:** NMR, cottonseed oil, methanol, ethanol, propanol-1, propanol-2.
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1. Introduction

The high industrialization of the world causes an increase in the use of fossil fuels. This has led to serious environmental problems such as the depletion of fuel reserves, an increase in the amount of CO_x, NO_x, and SO_2 gases in the air, and the greenhouse effect [1–20]. In the world literature, there are different scientific studies related to research on green chemistry, including green energy. These are mainly research projects such as natural fuel components, hydrogen, wind, solar energy, biomethanol, bioethanol production, etc. In developed countries such as America, Canada, France, Germany, Indonesia, Malaysia, etc., the production of these types of energy is increasing day by day. The Russia-Ukraine conflict has also increased interest in this area. Finding alternative fuel sources is quite promising for solving these problems.

One of the renewable energy types is biodiesel. Biodiesel, the most promising alternative fuel type for diesel engines, is non-toxic, biodegradable, and has the potential to greatly reduce environmental pollution. The main reaction type in biodiesel production is transesterification. Transesterification is a process that causes changes in the molecular structure of vegetable oils, reducing their viscosity and degree of unsaturation [2, 5]. One avenue of significant interest in biodiesel production involves the effective use of small-molecule alcohols and oils as feedstocks, presenting a pathway towards enhanced sustainability and economic viability. While methanol has been the primary alcohol employed in biodiesel production, ethanol has gained attention as an alternative due to its renewable sourcing from biomass and lower toxicity. The use of non-edible vegetable and waste oils has increased interest in the production of this type of fuel [4-9].

The selection of appropriate alcohol mixtures for biodiesel production necessitates a comprehensive understanding of their physicochemical properties, reaction kinetics, and compatibility with various feedstocks and catalysts. Furthermore, process optimization strategies are vital to maximize the yield, purity, and quality of biodiesel while minimizing energy consumption and environmental impact. Additionally, the economic viability of biodiesel derived from alcohol mixtures depends on factors such as feedstock availability, production costs, market demand, and policy incentives [21-22].

In this manuscript, we aim to review the current state of knowledge regarding biodiesel production using alcohol mixtures as feedstocks. Taking into account the above, the effect of low-molecular-weight alcohol mixtures on the transesterification reaction was studied for the first time in the presented work.

2. Experiments

Synthesis of biodiesel

Firstly, transesterification of propanol-1 and cottonseed oil in the presence of alkali was carried out. However, this reaction did not occur in the presence of alkali. Sulfuric acid was then used as a catalyst. The reaction was carried out at H_2SO_4 acid concentrations of 0.5-1 ml (2-4 %, relative to the oil). The same procedure was then repeated with isopropanol. The synthesis of biodiesel was based on cottonseed oil (25 ml), methanol:propanol-1:propanol-2 (34:33:33%), ethanol:propanol-1:propanol-2 (34:33:33%) alcohol mixtures, at 75 ^{0}C for 8 hours, considering the large reserves in our country. After the reaction product is separated in the separator funnel, it is washed with 80 ^{0}C water. Since the acid catalyst is used, it is easy to clean and no saponification is observed. The neutrality of the medium was controlled by litmus paper. The obtained biodiesels were dried in the presence of Na_2SO_4 (yielding 80 and 83%, respectively). Synthesis and separation processes are shown in figure (1).

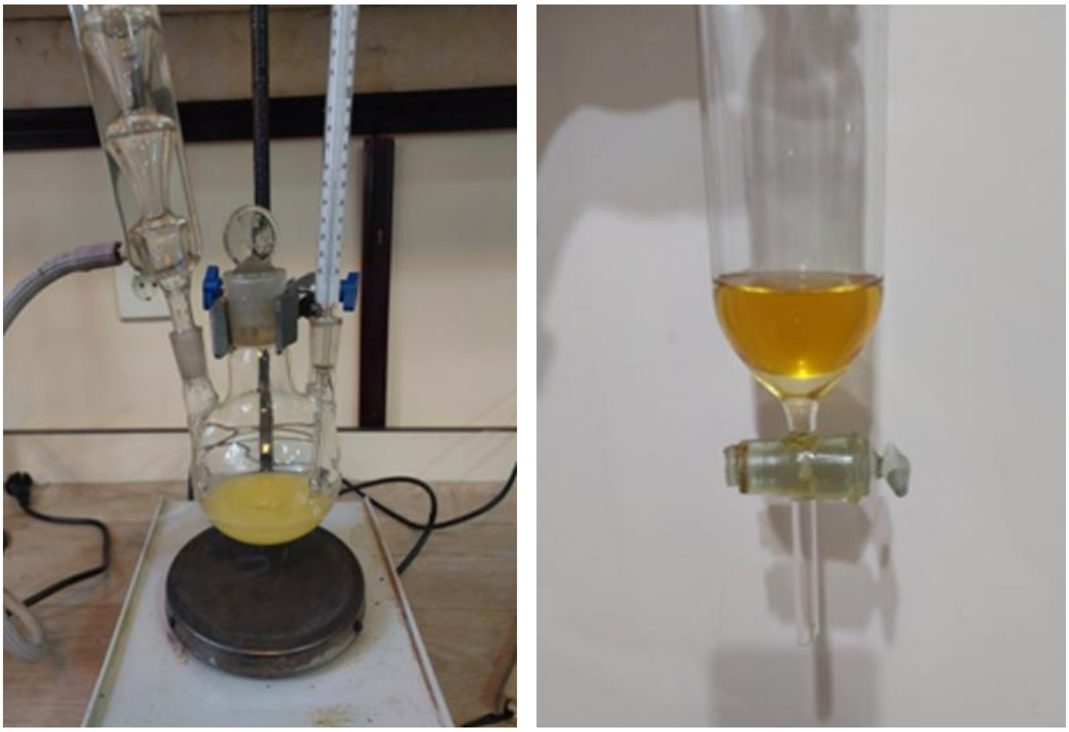
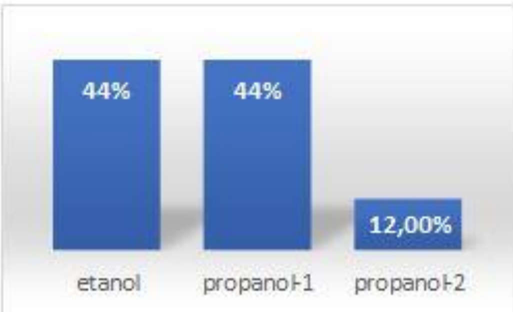


Figure 1. Synthesis and separation of biodiesel

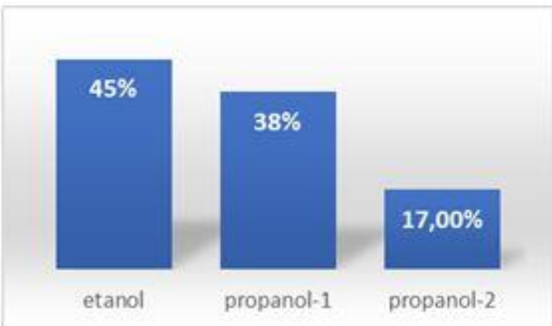
3. Results and discussion

In biodiesel production, the most common types of alcohols are methanol, ethanol, propanol, and butanol. As the molecular mass increases in this order, the yield of biodiesel decreases. The use of higher molecular weight alcohols complicates the reaction conditions. Additionally, branched alcohols (such as isopropanol) can be used, which has been observed to lower the cloud and pour point of the resulting biodiesel. The value of biodiesel fuel varies depending on factors such as feedstock availability, geographical location, seasonal variations in crop cultivation, crude oil prices, and so on. To investigate the effect of catalyst nature on the process, transesterification was conducted with alkali and acid catalysis. Initially, KOH and NaOH were used as the primary catalysts, but targeted results were not achieved with isopropanol, and biodiesel with a lower yield was obtained using propanol-1. It may be connected to an increase in viscosity as a result of the formation of more stable alcoholates in the reaction medium.

Subsequently, research continued with acid catalysis, and the influence of various concentrations of sulfate catalyst on the transesterification process was monitored. It was observed that with propanol-1 in the presence of the sulfate catalyst, a mixture of biodiesel and dipropyl ether (B100:DPE=70:30) was obtained with a catalyst concentration of up to 0.5% relative to the oil, while pure biodiesel was obtained at concentrations of 0.5–1%. With propanol-2 and a sulfate catalyst, higher yields of biodiesel were observed at a concentration of 0.5% relative to the oil. No increase in biodiesel yield was observed at sulfate concentrations below 0.5% or above 1%. Summarizing the above, we can note that biodiesel was synthesized based on a mixture of various low-molecular-weight alcohols to achieve raw material savings, increase diversity, and simultaneously investigate the effects of alcohol blends on the properties of biodiesel. Thus, the reaction was conducted for 8 hours using a mixture of methanol (ethanol) (34%), propanol-1 (33%), propanol-2 (33%), and cottonseed oil in the presence of H_2SO_4 as a catalyst. When the obtained biodiesel samples were examined by NMR spectroscopy, different participation rates of alcohols in the reaction were observed (scheme 1 and 2):



Scheme 1. Participation rates of methanol, propanol-1 and propanol-2



Scheme 2. Participation rates of ethanol, propanol-1 and propanol-2

As seen from schemes 1, 2 and figure 1, 2, methanol (M, 44%), propanol-1 (P1, 44%), propanol-2 (P2, 12%), as well as ethanol (E, 45%), propanol-1 (P1, 38%), and propanol-2 (P2, 17%), participate in the reactions. Additionally, the properties of biodiesel obtained from all alcohol mixtures were determined according to ASTM standards. The obtained results are presented in tables 1 and 2.

Properties	**B100 (E+P1+P2)**	**B10 (E+P1+P2)**	**B100 (M+P1+P2)**	**B10 (M+P1+P2)**
Density at 20^{0}C, g/cm^3	0.8769	0.8675	0.8782	0.8695
Viscosity at 20^{0}C, mm^2/s	7.300	4.950	7.057	4.913
Viscosity at 40^{0}C, mm^2/s	4.721	3.157	4.404	3.134
Flash point, ^{0}C	158	82	156	80
Cloud point, ^{0}C	+1	-10	+4	-8
Pour point, ^{0}C	-4	-27	-1	-22

Table 1. The exploitation properties of biodiesel fuel blends based on methanol, propanol-1 and propanol-2 alcohols

Properties	**Biodiesel (P1)**	**Biodiesel (DPE)**	**Biodiesel (P2)**	**B10 (P1)**	**B10 (DPE)**	**B10 (P2)**
Density at 20 ^{0}C, g/cm^3	0,8802	0,8770	0,88238	0.8578	0.8556	0.8609
Viscosity at 20^{0}C, mm^2/s	7,413	7,3605	10,251	5.340	5.316	5.785
Viscosity at 40^{0}C, mm^2/s	4,734	4,6165	6,210	3.295	3.283	3.356
Flash point, ^{0}C	190^{o}C	180^{o}C	198 ^{o}C	97	96	104
Cloud point, ^{0}C	+3^{o}C	+4^{o}C	+6 ^{o}C	-8, -9	-8, -9	-7, -9
Pour point, ^{0}C	-4^{o}C	-5^{o}C	-8 ^{o}C	-26	-20	-27

Table 2. The exploitation properties of biodiesel fuel blends based on propanol-1 and propanol-2 alcohols

According to tables 1 and 2, we can note that B10 fuel blends demonstrated excellent exploitation properties, such as viscosity at 40 ^{0}C (3.134 and 3.157 mm^2/s), flash point (80 and 82 ^{0}C), and pour point (-22 and -27 ^{0}C).

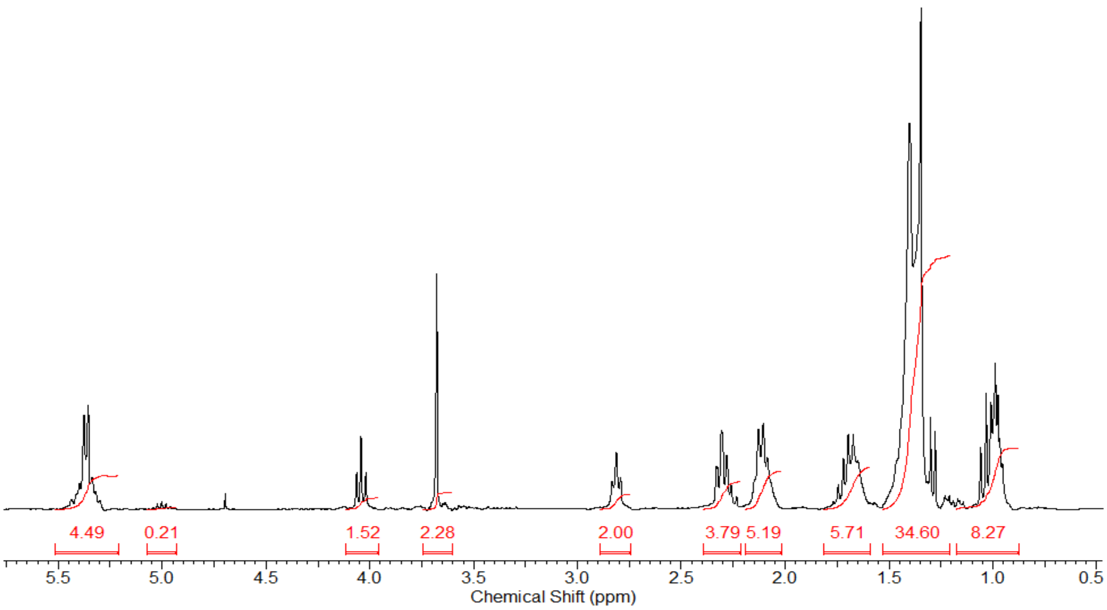


Figure 2. ^{1}H NMR spectrum of biodoesel from methanol, propanol-1 and propanol-2

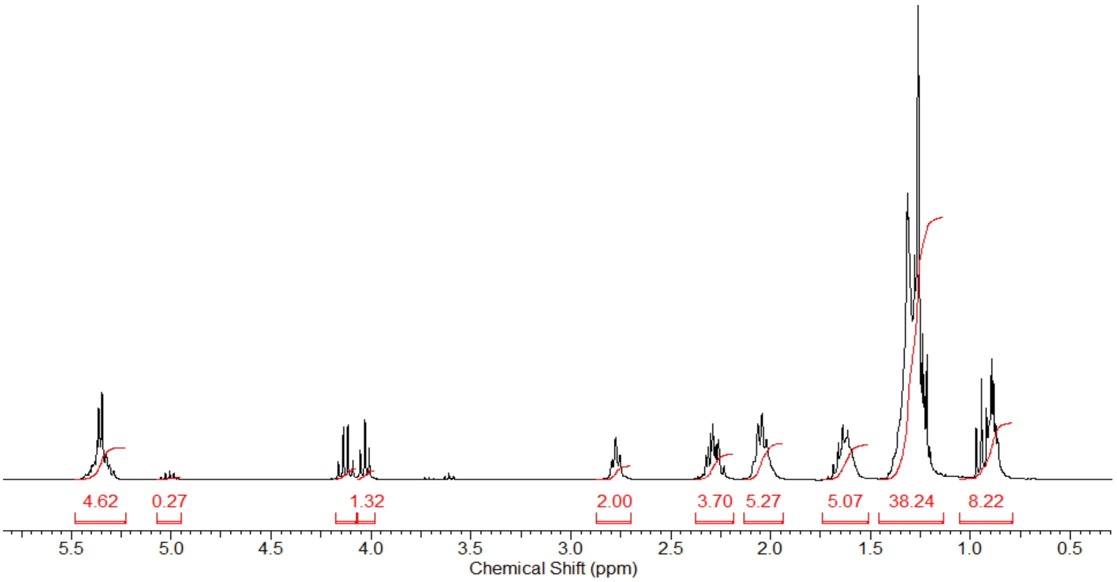


Figure 3. [1]H NMR spectrum of biodoesel from ethanol, propanol-1 and propanol-2

4. Conclusion

In this study, the effect of alcohol blends on the properties of biodiesel was investigated. Recently, alternative biofuels based on vegetable oils and derivatives have become increasingly widespread. Biodiesel fuel has characteristics such as low emission capacity, biodegradability, high lubricity, high cetane number, etc., which contribute to long engine life. This type of fuel can be used both in pure form and mixed with diesel fuel in different proportions in diesel engines. The main objective of this study is to obtain biodiesel from low molecular weight alcohols, prepare their mixtures, improve their performance, and enhance their ecological properties. The results obtained during the research can be successfully applied in the future for the synthesis and exploitation of ecologically clean biofuels based on local raw materials.

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Authors' Declaration
The authors declare no conflict of interest regarding the publication of this article.

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