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ULTRASONICALLY ASSISTED PREPARATION OF BIO-DIESEL FUEL AS CLEAN ENERGY FOR GLOBAL WARMING AND EMMISION OF FINE PARTICULATE MATTER

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KEYWORDS

Base catalysis, diesel fuel, transesterification, ultrasound, vegetable oil

ABSTRACT

Vegetable oils are produced from plants, their burning leads to a complete recyclable CO_2. The oil use as diesel fuel was limited due to its high viscosity (near 10 times of the gas oil). In order to adapt the fuel to the existing engines the vegetable oils had to be modified[1-7]. Vegetable oil contains no aromatic hydrocarbon and sulphuric compound, therefore the exhaust gas from diesel engine. The transesterification of vegetable oil with short-chain alcohols, in the presence of base-catalyst, by means of low frequency ultrasound (28 kHz and 40 kHz) was studied to produce clean fuel for global warming and emission of air pollutants. By using ultrasounds the reaction time is much shorter (10-40 minutes) than for mechanical stirring. The quantity of required catalyst is 2 or 3 times lower. The amount of alcohol used is only 6:1 molar ratio. Normal chain alcohols react fast, while secondary and tertiary alcohols show some or no conversion after 60 minutes of reaction. Surprisingly, 40 kHz ultrasounds are much more effective in the reduction of the reaction time (10 to 20 minutes). 28 kHz give slightly better yields (98-99%), but longer reaction time, while higher frequencies are not useful at all for the transesterification of fatty acids.

EXPERIMENTAL

Sodium hydroxide (95%) and potassium hydroxide (85%) were purchased from Wako Chemicals and used after milling, to facilitate the dissolution in alcohol. The alcohols employed in the reactions (methanol, ethanol, *n*-propanol, *iso*-propanol, *n*-butanol, *iso*-butanol, *tert*-butanol), from Wako Chemicals had more than 99.5% purity and were used as received. The vegetable oil was of commercial edible grade and it had the following basic properties: Acid value = 1.247 , Iodine value = 70, Saponification value =195.

Samples were taken at 10 minutes time intervals and analyzed by TLC (eluent chloroform/petroleum ether, 1:3 ratio) to check the conversion to biodiesel. After purification the biodiesel was analyzed using a Shimadzu GC-MS Model QP-2010, equipped with a DB-5 capillary column (0.53 mm x30 m) J&W Scientific.For methyl esters the mean molecular weight was 293.65. The mean molecular weight of the oil was calculated averaging the individual molecular weights of each constituent triglyceride, according to the fatty esters analysis. The average molecular weight of the oil was 878.23.

The reaction mechanism was formulated as a three-step reaction . The first step involves the

reaction between the triglyceride (TG) and one molecule of alcohol, leading to two diglyceride (DG1 and DG2) and one molecule of ester. The second step is the reaction of the diglyceride with a second molecule of alcohol, leading to two monoglyceride (MG1 and MG2) and another molecule of ester, and the third one the reaction of monoglyceride with the third molecule of alcohol leading to glycerin and ester. The secondary alcohols show some conversion under ultrasonic irradiation, while under stirring the transesterification does not take place. Tertiary alcohols have no conversion in both types of activation. We assume that this behavior is due to the sterical hindrance that impedes the access towards the reaction center, or in some case the access is limited, that makes the reaction rate very slow compared with normal-chain alcohols. Thus, from two competing reactions, i.e. saponification and trans-esterification, the first one takes place more rapidly, consuming the oil and catalyst and leading to soap formation.
In the table 1 the yields of isolated methyl esters for different types of activation in the presence of NaOH as catalyst are given.

Table 1. The yields of isolated methyl esters

	0.5% (wt/wt) NaOH		1.0% (wt/wt) NaOH		1.5% (wt/wt) NaOH	
Method	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
Mechanical stirring	60	**80**	10	**91**	10	**35**
Ultrasonic 28 kHz	40	**98**	10	**95**	10	**75**
Ultrasonic 40 kHz	20	**98**	10	**91**	10	**68**

From the results we can point out that under ultrasonic irradiation at 40 kHz frequency the reaction was complete faster. The best yields were obtained when the catalyst was used in small concentration, i. e. 0.5 % wt./wt of oil.

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