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Influence of reaction conditions and type of alcohol on biodiesel yields and process economics of supercritical transesterification

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ABSTRACT

Experiments with transesterification of rapeseed oil in supercritical alcohols (methanol, ethanol and 1-propanol) were carried out in a batch reactor at various reaction temperatures (250–350 °C), working pressure (8–12 MPa), reaction time, and constant 42:1 alcohol to oil molar ratio. Influence of different alcohols and reaction conditions on biodiesel yield was investigated using linear multiple regression models. Temperature had the highest impact on yields, followed by reaction time and pressure. With increased molecular weight of alcohols, relative importance of temperature for explanation of yields decreased and relative importance of time and pressure increased. Economic assessment has revealed that transesterification in supercritical methanol has the lowest direct material and energy costs. Yield has crucial impact on process economics. Direct costs decrease with increase in biodiesel yields. Even at very low prices of oil feedstock the lowest cost is achieved at the highest yield.

1. Introduction

Biodiesel has the potential to decrease greenhouse gas emissions and the dependence on foreign fuels; however, it still struggles to become competitive with fossil diesel fuels regarding the cost-effectiveness. The main reason for this is the high cost of refined vegetable oils currently used for the biodiesel production [1–3]. Conventional base catalytic processes used for biodiesel production cannot make use of feedstock with the presence of high amounts of free fatty acids (FFAs) and water. These impurities react with catalysts and lead to side formation of soaps which reduce the yields and make the separation of biodiesel from glycerol difficult [4–6]. Therefore, not more than 0.5 wt% FFAs and 0.06 wt% water are allowed in feedstock in order to ensure high yields [7]. Processes with acid catalysts have higher tolerance to the level of FFAs in the feedstock, but they require very long reaction time to achieve high yields, and the feedstock oil and alcohol must be essentially anhydrous [8].

Transesterification in supercritical alcohol was investigated as an alternative to conventional biodiesel production methods [9–14]. Transesterification in supercritical alcohol is a reaction without the presence of a catalyst in the process. In this method the temperature and pressure of the reactants reach up to the critical temperature and pressure of the alcohol. In these conditions the dielectric constants of alcohols are significantly lower, and they approach the dielectric constants of non-polar substances such as fats and oils. This creates a predisposition to a single-phase system of oil and alcohol. In addition, ionic product of alcohol increases with increased pressure, thus it is assumed that alcohol in supercritical conditions is not only a reactant but also an acidic catalyst [15–17]. These characteristics of transesterification in supercritical conditions make it possible to use oils with high FFA content (up to 36 wt%) at high conversion and reaction rates. Other advantages are good tolerance to water in feeds (up to 30 wt%), without reducing yields and reaction rates [16], and simpler separation and purification steps of biodiesel due to absence of catalyst in the process [18].

There are many investigations on the supercritical transesterification process concerning reactivity and kinetics [3,19–22]. Besides technical aspects, economic feasibility is also of great importance for assessment of process viability. Economic feasibility of biodiesel production in supercritical conditions has been evaluated by several authors with varying results and often contradictory conclusions [23–25]. Marchetti et al. [24] claim that supercritical transesterification is not cost competitive due to relatively high investments and consumptions of energy and alcohol, whereas others argue that it can compete with the existing alkali and acid catalyzed homogenous processes [24,25]. These investigations have focused on

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transesterification in supercritical methanol and there is no research, to our knowledge, which compared the effects of different reaction conditions and different types of alcohol on the economic performance of the process. Furthermore, these estimations are mainly based on information obtained from a process simulator, which do not necessarily coincide with empirical results. The choice of alcohol would not just influence the performance of reaction, but the fuel properties as well. Several researchers have shown that usage of 1-propanol instead of methanol in the transesterification process can significantly lower the pour point and cold filter plugging point of biodiesel [26,27] and improve its performance in the winter period.

The present work focuses on an economic evaluation of transesterification of rapeseed oil in supercritical alcohols (methanol, ethanol and propanol) using the experimental setups with batch regime. The effects of temperature, pressure, reaction time and type of alcohol on biodiesel yields and production costs were investigated.

2. Materials and methods

2.1. Raw material characterization

Cold-pressed oil of a Serbian oilseed rape (the Kata variety) was applied in the experiment. Kata is a winter oilseed rape from the "00" maturity group (low erucic acid and glucosinolates) which makes the oilcake suitable as animal feed. This is the first genotype of oilseed rape with high oleic acid content in oil in Serbia. Physical and chemical properties of the obtained oil are given in Table 1.

During the experiments, three different alcohols (methanol, ethanol and 1-propanol) were used. Characteristics of the used alcohols are given in Table 2.

2.2. Equipment and experimental procedure

Transesterification of rapeseed oil in different alcohols was carried out in a batch reactor (Anton Parr 4520). The reactor had a volume of 2 dm^3, with the possibility of mixing the oil and alcohol with an anchor stirrer. The reactor was also equipped with an electric heater, which allows heating the mass up to 350 °C, Fig. 1.

Rapeseed oil was mixed in the reactor with alcohol (methanol, ethanol or 1-propanol) in a molar ratio of 1:42 and heated to temperatures of 250, 300 and 350 °C. Previous researches suggest that in supercritical conditions maximum yields are reached at around 1:42 oil to alcohol molar ratio [12,20]. After reaching the desired temperature of the oil and alcohol mixture (within ±2 °C), the reactor was flushed with nitrogen (99.8% purity, Messer) at constant pressure of 8.1, 10 and 12 MPa. The reaction was conducted until the time when a decrease in the yield was observed, i.e. after the equilibrium was reached. The equilibrium is defined at the point where maximum yield is achieved in function of time for the particular combination of reaction temperature and pressure. After the specified reaction time, the mixture was cooled down to a temperature of about 150 °C. After reaching this temperature, the unreacted alcohol was removed from the reaction vessel. Alcohol vapour in nitrogen flow was passed through a 3.5 m long, water-cooled condensing column. After further cooling of the reaction mixture to a temperature of about 55 °C, the reaction mixture was introduced into the separation vessel for ageing for 16 h. After separation of raw biodiesel, the same was subjected to vacuum distillation to remove the residual alcohol.

The experiment was designed as an incomplete three factor factorial design. Two factors, temperature and pressure, have three levels. The number of levels of the third factor, reaction time, varies depending on the time needed to achieve the equilibrium state for the particular combination of temperature and pressure (Table A.1). The experimental results were obtained by variation of transesterification conditions. For each of the combination of reaction time, pressure and temperature three replicates were done and the average yield was calculated. In all experiments the esters yield (E_{Yield}) was calculated by the following equation:

$$E_{Yield} = \frac{\text{Amount of ester layer (g)} \cdot \text{Purity of ester layer (\%)}}{\text{Amount of edible oil, feedstock (g)}} \ (\%) \quad (1)$$

After decanting, all product samples were weighed and the amount of ester was identified. Yield was obtained as a function of purity of ester layer by involving the values of the ester amount and the amount of edible oil in (1). The obtained biodiesel was subjected to Gas chromatograph (GC) analysis to determine the content of fatty acid esters (FAE) (according to SRPS EN 14103).

The used amount of electricity needed to heat the reaction mixture and to maintain the desired temperature in reactor was measured by an electricity counter (Tracon Electric TVO-F1-1).

2.3. Statistical analysis

For each type of alcohol the effect of temperature, pressure, and time on the biodiesel yield was analyzed using linear multiple regression model. Standardized regression coefficients (or beta weights) are the most common measure of relative influence of predictors on a dependent variable. For the linear regression model with p predictor variables standardized coefficients can be expressed as:

$$b_i' = \frac{S_Y}{S_{X_i}} \cdot b_i, \ (i = 1, \ldots, p), \quad (2)$$

where b_i, $(i = 1, \ldots, p)$ are the least squares estimates of regression coefficients, S_Y and S_{Xi} are sample estimates of standard deviations of variables Y and X_i, $(i = 1, \ldots, p)$.

It is important to note that standardized regression coefficients should be used to compare the effects of variables within equations. They can never be compared across samples or populations because the standardization is different for each group.

The main focus of analysis is in obtaining relative importance as proportionate contribution of each predictor to coefficient of determination (R^2) considering both the unique contribution (direct effect) of each predictor by itself and its effect when it is combined with other predictors. Six different metrics for assessing relative importance of regressors in the linear regression models are given

Table 1
Physical and chemical properties of rapeseed oil used as raw material.

Characteristic	Unit	Value	Method
Density (20 °C)	g cm^{-3}	0.9068	SRPS EN ISO 3675
Viscosity (40 °C)	mm^2 s^{-1}	32.11	SRPS EN ISO 3104
Water content	%	0.01	SRPS ISO 665 and 662
Acid value	mgKOH g^{-1}	2.91	SRPS ISO 660
Solid content	%	0.32	SRPS ISO 663
Molar mass	g mol^{-1}	881.5	
Iodine value	gJ 100 g^{-1}	107.934	EN 14214
Fatty acid composition			
Myristic (C14:0)	wt%	0.076	
Palmitic (C16:0)	wt%	4.75	
Stearic (C18:0)	wt%	1.496	
Oleic (C18:1)	wt%	66.955	
Linoleic (C18:2n6c)	wt%	16.79	
Linolenic (C18:3n3)	wt%	7.803	
Arachidic (C20:0)	wt%	0.495	
Eicosenoic (C20:1)	wt%	1.043	
Behenic (C22:0)	wt%	0.37	
Erucic (C22:1n9)	wt%	0.057	
Lignocerinic (C24:0)	wt%	0.166	