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ScienceDirect
Bioresource Technology 98 (2007) 2688–2699
BIORESOURCE TECHNOLOGY

The effect of agitation intensity on alkali-catalyzed methanolysis of sunflower oil

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Received 27 June 2006; received in revised form 11 September 2006; accepted 17 September 2006
Available online 7 November 2006

Abstract

The sunflower oil methanolysis was studied in a stirred reactor at different agitation speeds. The measurements of drop size, drop size distribution and the conversion degree demonstrate the effects of the agitation speed in both non-reaction (methanol/sunflower oil) and reaction (methanol/KOH/sunflower oil) systems. Drop size distributions were found to become narrower and shift to smaller sizes with increasing agitation speed as well as with the progress of the methanolysis reaction at a constant agitation speed. During the methanolysis reaction, the Sauter-mean drop diameter stays constant in the initial slow reaction region, rapidly decreases during the fast reaction period and finally reaches the equilibrium level. Due to the fact that the interfacial area increases, one can conclude that the rate of reaction occurring at the interface will also be enhanced progressively. The ‘‘autocatalytic’’ behavior of the methanolysis reaction is explained by this ‘‘self-enhancement’’ of the interfacial area, due to intensive drop breakage process.

Keywords: Biodiesel; Kinetics; Methanolysis; Sunflower oil; Sauter-mean diameter

1. Introduction

Biodiesel has attracted considerable attention among many researchers as an alternative fuel for diesel engines, due to the depleting fossil fuel resources and its favorable properties. First of all, it is made from renewable biological sources, such as vegetable oils and animal fats, which react with an alcohol in the presence of a catalyst. As further advantages of biodiesel, one should emphasize that this fuel is biodegradable, non-toxic and with low emission profiles as compared to petroleum-based diesel fuel. Chemically, biodiesel is a mixture of alkyl esters of long chain fatty acids, produced in the reaction called alcoholysis.

The alcoholysis process is affected by a number of factors, but the most important are as follows: type and concentration of catalyst, type of alcohol, molar ratio of alcohol to vegetable oil, reaction temperature, presence of free fatty acids and moisture and agitation intensity. The effects of these factors on the kinetics of alcoholysis are critically discussed in several reviews (Fukuda et al., 2001; Ma and Hanna, 1999; Schuchardt et al., 1998; Stamenković et al., 2005).

The agitation intensity appears to be of a particular importance for the alcoholysis process. The mass transfer of triglycerides from the oil phase towards the methanol–oil interface could be a critical step limiting the rate of alcoholysis reaction because the reaction mixture is heterogeneous, consisting of two immiscible phases. Poor mass transfer between two phases in the initial phase of the reaction results in a slow reaction rate, the reaction being mass transfer controlled (Noureddini and Zhu, 1997). Beside this, the low solubility of methanol in the vegetable oil

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doi:10.1016/j.biortech.2006.09.024

Nomenclature

a	specific interfacial area, m^2/m^3
d_{av}	arithmetic-mean drop diameter, m
d_i	drop diameter, m
d_{max}	maximum stable drop diameter, m
D_i	impeller diameter, m
d_{32}	Sauter-mean drop diameter, m
n	agitation speed, s^{-1}
n_i	number of drops with diameter d_i
Re_i	impeller Reynolds number, 1
Greek symbols	
α	multifractal exponent, Eq. (8), 1
β	exponent on agitation speed, Eq. (7), 1
φ	holdup of dispersed phase, 1
μ	viscosity, Pa s
ρ	density, kg/m^3
Subscripts	
c	continuous phase
d	dispersed phase
e	emulsion
m	minimum

can limit the rate of alcoholysis reaction during its early stages (Boocock et al., 1996).

The alkali-catalyzed alcoholysis kinetics of soybean oil (Freedman et al., 1984, 1986; Noureddini and Zhu, 1997), palm oil (Darnoko and Cheryan, 2000), rapeseed oil (Komers et al., 2002) and sunflower oil (Vicente et al., 2005) has been studied. So far, the effect of agitation speed on the alkali-catalyzed alcoholysis has been investigated in a few studies. A survey on operating conditions applied in studying kinetics of alcoholysis reaction and effects of agitation intensity on it is given in Table 1. Different types of agitators and a range of agitation speeds were applied in these studies, but only in a few of them the importance of drop size distribution has been recognized. Different vegetable oils, such as soybean, rapeseed, sunflower and palm oil, as well as melted beef tallow, are used as sources of triglycerides for the process of alcoholysis. Methanol was used as the second reactant, the most often molar ratio of methanol

Table 1
A survey of operating conditions applied in studies on the effects of agitation intensity on the kinetics of alkali-catalyzed methanolysis in batch reactors at atmospheric pressure

Oil	Reactor volume/ diameter, mL/cm	Type/diameter of agitator, cm	Agitation speed, rpm	Molar ratio of methanol to oil	Catalyst/ quantity, % of oil	Temperature, °C	Reference
Soybean	400; five-necked flask	Mechanical stirrer	–	6:1	Sodium methoxide 0.5	20–60	Freedman et al. (1986)
Sunflower	250/4.5	Magnetic stirrer/4.0	400	3:1 and 3.3:1	KOH 0.75–2.0	25 (40 and 60)	Mittelbach and Trathnigg (1990)
Soybean, edible	1500 (300)[a]	Mechanical stirrer	150–600	6:1	NaOH 0.2	30–70	Noureddini and Zhu (1997)
Soybean, edible	–[b] 600	Two motionless mixers and a high-shear mixer	0–2700	6:1 and 8:1	NaOH 0.1–1.0	80[c]	Noureddini et al. (1998)
Melted beef tallow, edible	450[a]/6.35	Turbine	110, 220 and 330	6:1	NaOH 0.3[d]	80	Ma et al. (1999)
Soybean, edible	2000 (1117)[a]	Anchor	300 600	6:0.8	Sodium methoxide 1.0[d]	60	Alcantara et al. (2000)
Palm, refined	1000; three-necked flask	Magnetic stirrer	–	6:1	KOH 1.0	55–65	Darnoko and Cheryan (2000)
Rapeseed	243–320[a]	Magnetic stirrer	–	1:1–6:1	KOH 0.29–1.59	22.7	Komers et al. (2002)
Sunflower, edible	2000 (1000)[a]	Rushton turbine/10	80–1000	6:1	NaOH 0.5[d]	Room	von Blottnitz et al. (2004)
Sunflower, edible	250 (125)[a]; three-necked flask	Helix	300–700	6:1	KOH 0.5–1.5	25–65	Vicente et al. (2005)
Sunflower, edible	1000 (410 or 820)[a]/10	Two flat-blade paddle/7.5	60–200	6:1	KOH 1.0[d]	20	This work

[a] Operating volume.
[b] Continuous process.
[c] Carried out at 172 kPa.
[d] Prepared freshly.