Fuel Processing Technology 125 (2014) 34–40

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Kinetics of reactive extraction/in situ transesterification of rapeseed oil

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ARTICLE INFO

Article history:
Received 30 August 2012
Received in revised form 25 September 2013
Accepted 16 March 2014
Available online 6 April 2014

Keywords:
Biodiesel
Rapeseed
Canola
Kinetics
Reactive extraction
In situ transesterification

ABSTRACT

The kinetics of "reactive extraction" or "in situ transesterification" of rapeseed with methanol to produce biodiesel were investigated. It is hypothesised that in situ transesterification occurs through the reaction of triglyceride and methanol inside the seed particles followed by diffusion of mono and diglycerides, esters and glycerol into the bulk solvent. A model was developed based on this reaction/extraction mechanism and was found to be generally consistent with experimental results. The effective diffusion coefficient of esters in methanol was found to be 3.5×10^{-12} m^2/s. The model reveals that at catalyst concentrations below 0.1 mol/kg-solvent, the reactive extraction rate was controlled by the reaction of triglycerides to esters. However, at higher catalyst concentrations (>0.1 mol/kg-solvent), the process was controlled by the rate of diffusion of the products. The diffusion coefficient increases linearly with increasing temperature and the temperature dependence of the reaction rate constants can be described by an Arrhenius relationship. External mass transfer does not influence the extraction rate at the conditions used in these experiments.

Nomenclature

A_p	particle surface area	m^2
C_A	concentration of species A inside the particle	mol/L
$C_{A,b}$	concentration of species A in the bulk solvent	mol/L
$C_{A,s}$	concentration of species A at the particle surface	mol/L
d_p	average particle diameter	m
D_{eff}	effective diffusivity	m^2/s
D	diffusion coefficient	m^2/s
E_a	activation energy	J/mol
k	reaction rate constant	L/mol/s
$k_{m,A}$	external mass transfer coefficient of species A	m/s
k_o	Arrhenius constant	L/mol/s
n_A	moles of species A in the particle	mol
N_p	number of particle	
r	radius inside seed particle	m
r'_A	reaction rates of species A	mol/L/s
$r'_{A,b}$	reaction rates of species A in the bulk solvent	mol/L/s
r_m	mean radius between r and delta r	m
R_O	outer radius of seed particle	m
R	universal gas constant	
Re	Reynolds number	
Sh	Sherwood number	
Sc	Schmidt number	
t	time	s
T	temperature	K
V_b	solvent volume	m^3
W_A	flux of species A	mol/m^2
ε	porosity	

1. Introduction

Biodiesel is a fuel derived from renewable resources, in practice largely edible and inedible oil-bearing seeds, palm fruits and waste cooking oil. Biodiesel can be considered as a versatile fuel making it an attractive alternative to petroleum diesel. It is most commonly produced by the reaction of vegetable oils with an alcohol to produce fatty acid alkyl ester. The fuel can be readily used in most diesel engines without any modification and engine performance has been shown to be comparable to that of conventional diesel fuel [1]. The use of biodiesel reduces the emission of carbon monoxides, particulates and hydrocarbon from the engine [1]. Furthermore, a biodiesel blend has lubricating properties that can reduce engine wear and extends engine life [2,3].

In the conventional biodiesel process, the first step is the extraction of the oil from the plant or animal sources followed by transesterification with an alcohol to produce fatty acid alkyl ester. Extraction of the oil is commonly performed using solvents such as hexane or dichloromethane, which have high affinities for triglycerides. Mechanical pressing is also commonly used to extract the oil although it often yields less oil than solvent extraction resulting in a higher residual oil in the waste biomass. Once extracted, the oil may need to be purified before entering the transesterification unit. However, it has been demonstrated that the extraction and transesterification process can be performed simultaneously using a single alcohol, hence eliminating a separate extraction step and avoiding the use of solvents such as hexane [4]. This combined route, which is often termed "reactive extraction" or "in situ transesterification", has the advantages of simplifying the biodiesel production process as well as potentially reducing production cost.

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http://dx.doi.org/10.1016/j.fuproc.2014.03.019
0378-3820/

In reactive extraction or in situ transesterification, the biomass is directly reacted with the alcohol and a catalyst. The resulting extracts are mainly biodiesel and glycerol. The alcohol can be various short-chain alcohols such as methanol, ethanol or butanol, although methanol is commonly used due to its lower price and because it reacts the most rapidly. Methanol, however, is a poor solvent for triglycerides and is unable to extract most types of triglycerides to any significant extent [5,6]. However, when it is used in in situ transesterification, the oil is extracted directly as fatty acid methyl ester (FAME) [4]. The yield of FAME nonetheless greatly depends on the process parameters, such as catalyst concentration and methanol to oil molar ratio [7]. Since methanol is a poor solvent for triglycerides, the mechanism that allows a significant extraction of triglycerides and a subsequent transesterification to ester to take place during reactive extraction has not been definitively identified. Kildiran et al. (1996) suggested that the extraction of triglycerides is possible due to the stepwise dissolution and subsequent transesterification of the oil [8]. Haas et al. (2004) and Qian et al. (2008) proposed that the alkaline catalyst could destroy the cell walls and intracellular compartmentalization resulting in cellular solubilisation and subsequent transesterification of triglycerides [9,10]. On the other hand, the results from our previous studies show that most rapeseed cell walls of in situ transesterified seeds remain fully intact [11], and a shrinking core of oleaginous material is clearly visible. These findings strongly suggest that triglycerides reacted with the alkaline methanol in situ through a reaction between the diffused methanol and the small oil bodies inside the plant cell walls. Once the triglyceride has reacted, the reaction products (glycerol, FAME, mono- and diglycerides) which are soluble in methanol are able to diffuse from the seed internal into the bulk solvent. In this paper, a fundamental model is developed based on the suggested mechanism in order to simulate the reactive extraction process. The modelling of the process mechanism is important in predicting the effects of various process parameters and in providing insight into possible further process improvements.

2. Materials and methods

2.1. Reagents and material

The rapeseed was kindly provided by a local farm near Newcastle upon Tyne. The methanol used was of 99.97% purity. The solvent was purchased from Fisher Scientific. Methyl heptadecanoate and tricaprin internal standards were obtained from Sigma-Aldrich.

2.2. Reactive extraction

25 g of ground and sieved seed was placed in a 500 mL round-bottom flask equipped with a condenser and an overhead stirrer and placed in a constant temperature water bath. Alkaline alcohol, prepared by dissolving a known amount of sodium hydroxide in methanol, was first heated to the desired temperature using a heated circulating water bath. Once heated, 250 ml of the alcohol was transferred to the round-bottom flask and the reaction was carried out at 40, 50 and 60 °C until the desired reaction periods. The concentration of catalyst was 0.1 mol/kg-solvent. The stirrer speed was maintained at 200 rpm for all of the experiment. For the investigation on the effect of catalyst concentration, the concentration of catalyst was varied at 0.1, 0.05 and 0.03 mol/kg-solvent while the temperature was maintained at 60 °C.

To obtain the time profile of ester and the reaction intermediates, 0.5 mL samples of the reaction mixture were taken at different time intervals using a syringe and a tube from the sampling pots. 3 μL of glacial acetic acid was added to stop the reaction. A syringe filter was used to separate the liquid from the rest of the seed particles. A small portion of the liquid, which contains methanol and the reaction products, was analysed using a gas chromatograph in order to quantify the amount of ester in the bulk methanol phase. The rest of the liquid was evaporated to remove the methanol until the sample reached constant weight. The product was then allowed to settle into two layers and the ester phase was withdrawn from the top. The concentration of mono-, di- and triglycerides was quantified using a gas chromatograph/mass spectrometer (GC–MS).

2.3. Ester analysis

Gas chromatography analysis for the determination of individual and total esters was based on the British Standard BS EN 14103:2003, with some modifications. The internal standard used was methyl heptadecanoate (MHDN). The stock solution of the internal standards was prepared by adding 5 g of methyl heptadecanoate in 322.6 g methanol. A known amount of sample (1–2 g range) was weighed accurately into a sample vial with 1.25 g of the stock solution. The injection volume used was 0.2 μl. The gas chromatograph used was a HP 5890 Series II, with a Varian CP wax column with dimensions of 0.53 mm i.d., 10 μm coating thickness and 25 m length. The carrier gas was helium at a flow rate of 2 mL/min and the column, injector and detector temperature were maintained at 220 °C. The column separated the esters and the methyl heptadecanoate (MHDN) into individual peaks.

The weight percent of ester in the bulk methanol phase (C) was calculated using the equation below:

$$C = \frac{\frac{(100 - Area\ \ MHDN\%)}{Area\ \ MHDN\%} \times Solvent\ Ratio \times mass\ of\ standard\ used(g)}{Mass\ of\ sample\ used(g)}.$$

2.4. Gas chromatography/mass spectroscopy (GCMS) method for glyceride analysis

A GCMS was used to quantify the monoglycerides, diglycerides and triglycerides in the ester phase. The method was based on BS EN 14105 with some modification to the calibration procedure, in order to account for the higher glyceride content, which occurs particularly during the early reaction time. Tricaprin (1,2,3-tricaproylglycerol) was used as a basis to calibrate the glycerides.

For the analysis of monoglyceride, about 20 mg of sample was accurately weighed and placed in a sample vial. 20 μl of tricaprin stock solution (12.6 mg/mL) and 20 μL of N-methyl-N_trimethylsilyfluoraacetamide (MSTFA) were added to the sample vial. The solution was left to silylate for 15 min, after which 2 mL of heptane was added. For identification of TG and DG about 20 mg of sample was accurately weighed and place in a sample vial. 100 μL of tricaprin stock solution (0.5 mg/ml) and 20 μL of MSTFA were added to the sample vial. The solution was left to silylate for 15 min after which 0.5 mL of heptane was added. The GCMS was fitted with Perkin Elmer Col-elite column (PE-5HT) of 15 m length, 0.25 i.d. and 0.1 μm film thickness. The detector type in the mass spectrometer was electron impact positive. The flow rate of helium was 1 mL/min. The oven temperature protocol was 50 °C held for 1 min, heated to 180 °C at 15 °C/min, then at 7 °C/min to 230 °C and at 10 °C/min to 370 °C. The temperature was then held at 370 °C for 10 min for a total run time of 31.5 min. The inlet line to the MS was kept at 270 °C while the MS source temperature was kept at 250 °C.

3. Calculation/modelling

The reactive extraction of triglycerides and methanol to produce fatty acid methyl ester was modelled as the following steps:

1. Diffusion of methanol and catalyst through the seed external boundary layer to the particle surface.
2. Diffusion of methanol and catalyst into the seed to the surface of oil droplets.
3. Reaction of triglycerides with methanol within the seed particle.