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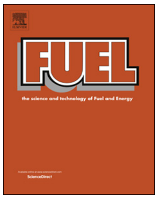

Full Length Article

In-situ FTIR study on the mechanism of both steps of zeolite-catalysed hydroesterification reaction in the context of biodiesel manufacturing

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ABSTRACT

While biodiesel manufacturing using transesterification is a mature process, a number of key issues need to be addressed for widespread application. These include amongst others feedstock availability and waste products. In this paper, we report on a different approach to synthesize biodiesel, namely a two-stage process which alleviates the need to utilise purified oils and only contains relatively pure glycerol as by-product. We investigated a route for waste cooking oil hydroesterification (hydrolysis/esterification) over zeolites. We tried to understand the mechanism of both steps of zeolite-catalysed hydroesterification and investigate the adsorption of probe molecules, along with the compounds formed by ester hydrolysis and fatty acid esterification reactions over the ZSM-5 zeolite surface by employing *in-situ* FTIR. The 40% conversion level of waste oil hydrolysis into fatty acid mixture and 63% conversion level of the synthesised fatty acids esterification to biodiesel was observed over ZSM-5 (Si/Al ratio = 15) after 4 h. The results from FTIR spectroscopy evident the protonation of the carbonyl groups of ester and fatty acid via hydrogen bonding with bridging OsbndH in SisbndOHsbndAl group (Brønsted acid sites) of the zeolite. The electrophilic reaction of protonated fatty acid, adsorbed on the surface of zeolite, with alcohol was observed from FTIR spectroscopy of esterification reaction.

1. Introduction

Hydroesterification involves hydrolysis of the oil feedstock in the first step and esterification of the free fatty acids (FFAs) produced in the second step, is a relatively new approach for production of biodiesel (Fatty Acid Methyl Ester (FAME)) from low-quality fatty substrates such as waste oils. Removal of impurities from the oil in the hydrolysis step results in a robust process which is insensitive to moisture content and low pH of feedstocks [1,2]. This process circumvents soap formation as major disadvantages of older but widely commercialised biodiesel production technique.

The hydrolysis reaction mostly occurs via a nucleophilic substitution in which an electron-deficient species (electrophiles) are attacked by an electron rich species (nucleophiles) [3]. Hydrolysis reaction can occur under various pathways, depending on the structure of the functional group of reactants and the products formed in the reaction. Autocatalytic behaviour has been suggested for ester hydrolysis and can be substantiated by the addition of FA to initial reaction mixtures [4,5]. Fischer esterification is the reaction of carboxylic acids with alcohol in presence of acid catalyst to form ester along with water [6]. FFA esterification reactions only take place over acid catalysts [7] and have a similar reaction mechanism as acid-catalysed transesterification [8]. Acetic acid esterification over all zeolite frameworks based on a detailed kinetic study [9,10] is suggested to follow an Eley-Rideal mechanism in which the reactant molecules are adsorbed on the zeolite active sites forming protonated acetic acid intermediates and an electrophilic intermediate react with alcohol in the next step. Chemical equilibrium is suggested to be rapidly attained for FA esterification reaction (equilibrium conversion level of 76% was achieved for oleic acid esterification with methanol at T = 110 °C [11]). These values can be substantiated employing the Gibbs free energy minimisation using UNIFAC [12] and modified Wilson [13] thermodynamic models that estimated 77% equilibrium conversion for same experimental condition.

In-situ Fourier transform infrared (FTIR) spectroscopy can characterise the functional groups present in a catalyst, and help understand the changes in functional groups as the catalyst is heated and catalysing reaction(s) [14]. FTIR spectroscopy analysis is a suitable technique to apply to hydroesterification studies, in order to gain an understanding of the mechanism of oil hydrolysis and FA esterification [15–18].

The present research study carried out experiments to identify the surface species present during zeolite-catalysed hydroesterification. *In-situ* FTIR spectroscopy was employed to determine i) the nature of the acid sites ii) the compounds formed during ester (ethyl acetate)

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Table 1
The structural parameters of ZSM-5 zeolites used in the experiments.

SAR	Langmuir surface area (m^2/g)	t-Plot micropore volume (cm^3/g)	Pore size (nm) [19]
15	410	0.09	0.51*0.55 0.53*0.56
140	450	0.12	

Table 2
Concentration of acid site of ZSM-5 zeolites used in the experiments determined from NH_3-TPD.

	SAR	Weak Brønsted (mmol/g)	Strong Brønsted (mmol/g)	Lewis (mmol/g)	T_{max} (°C)	ΔE_{des} (kJ/mol)
H-ZSM-5	140	0.10	0.17	0.00	428	191.53
	15	0.63	0.39	0.01	393	181.68

hydrolysis and iii) compounds present in FA (acetic acid) esterification reactions in the pores of the ZSM-5 zeolite.

2. Experimental section

2.1. Materials

The zeolite-catalysed hydrolysis reaction took place using waste cooking oil (provided from Biodiesel Industries Australia Pty Ltd Company, NSW, Australia) with distilled water and derived FAs (from the hydrolysis step) were used in the subsequent esterification reaction with ethanol (Fisher Scientific, 99.7%, CAS Number 64-17-5). The FTIR spectroscopy analysis were conducted using ethyl acetate (Fisher scientific, 99.9%, CAS Number 141-78-6), as hydrolysis surrogate reactant, with distilled water and acetic acid (Fisher Scientific, 99.7%, CAS Number 64-19-7) to be esterified using ethanol. Reactions were conducted over H-ZSM-5 zeolite with SAR = 15 (Zeolyst International, Ref. CBE3024E) and H-ZSM-5 zeolite with SAR = 140 (Zeolyst International, Ref. CBV28014). For porosity and surface area please see Table 1.

The products were separated from zeolite particles and the aqueous by-products with a centrifuge. Product samples for analysis were diluted in a solution of n-hexane (Sigma Aldrich, Anhydrous 95%, CAS Number 0110543). FAME standard solution (Sigma Aldrich, C8-C24 Lipid standards: FAME mixture) were used for identification and quantification of products peak in gas chromatography (GC) analysis. Our GC analysis shows that the composition of waste oil used in the experiments consists of mainly palmitic acid (45%), oleic acid (40%), linoleic acid (10%) and stearic acid (5%). The structural parameters and porosity of ZSM-5 zeolites were obtained from nitrogen physisorption analysis.

Temperature programmed desorption (TPD) of ammonia (NH_3) was employed to characterise the acidic properties of the catalysts (both number of acid sites on the catalyst and the relative strength of these acid site). Based on NH_3-TPD profiles, we have determined the concentration of weak Brønsted (W.B.), strong Brønsted (S.B.) and Lewis (L) sites for ZSM-5 zeolites used in experiments as is shown in Table 2. The heat of NH_3 desorption (ΔE_{des}), was also calculated based on the

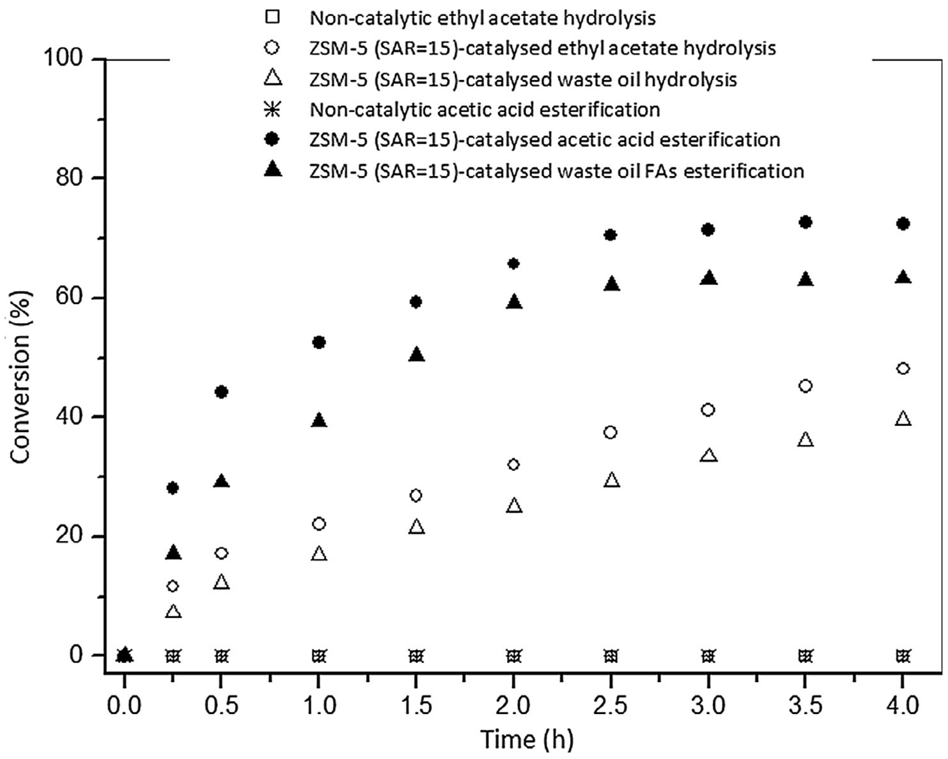

Fig. 1. Conversion level observed with time during non-catalytic and ZSM-5 (SAR = 15)-catalysed ester hydrolysis and FA esterification over ($T_{Hydrolysis}$ = 100 °C, $T_{Esterification}$ = 77 °C, stirring rate = 250 rpm, amount of catalyst = 5% w/w, water:ester volumetric ratio = 3:1, ethanol:FA molar ratio = 3:1).