Catalytic pyrolysis of vegetable oils to biofuels: Catalyst functionalities and the role of ketonization on the oxygenate paths

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ABSTRACT

Thermal and catalytic conversions of palm oil were investigated at 693 K. The conversions of acetic acid and ethyl acetate in the gas phase were also investigated over the same catalysts as model reactions. The acido-basicity of the catalysts was assessed by IR spectroscopy of adsorbed pyridine. Oxide catalysts slightly decrease the liquid yield, but allow the strong reduction of the production of saponifiable compounds, including fatty acids, in the liquid. The basic catalyst calcined hydrotalcite is the most effective in reducing saponifiables, but produces big amounts of heavy ketones (stearone and palmitone) according to its high activity in acid and ester ketonization. The Lewis acid catalysts alumina (strong) and Na-faujasite (weak) favor decarboxylation reaction, producing hydrocarbon rich liquids with significant amounts of olefins. The Brønsted acid catalyst H-ZSM-5 zeolite produces liquids richest in paraffins with some aromatics. However, the volatility range of the produced liquids is quite broad.

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1. Introduction

On the frame of a future industrial chemistry based on renewable feedstocks, the use of vegetable oils as biofuels or as precursors of biofuels represents an interesting perspective [1]. Non-edible oils, such as jatropha oil [2], used frying oils and oils derived from very productive oleaginous plants such as palm oil are possible candidates for this application. Vegetable oils could be used as such as fuels of diesel engines, but the combination of their high reactivity, density and viscosity, and poor volatility gives rise to a number of drawbacks [3,4]. The conversion of vegetable oils into biodiesel (fatty acid methyl esters, FAMEs) represents an established technology: however, further optimizations of the processes are under study [5], and the cost of refining the byproduct, glycerol, should be reduced [6]. Additionally, the FAMEs have considerable drawbacks, again due to high reactivity, poor stability [7] and cold properties.

As an alternative, hydrogenation processes of vegetable oils, like the NExBTL process from Neste Oil and the Ecofining process from ENI-UOP, have been developed at the commercial level and produce an excellent Green Diesel: however, they are very expensive, due to the need of hydrogen and high reaction pressure [8]. Also, the environmental friendliness of the process and the product really depends on the method with which hydrogen is manufactured.

A further option, still experimental, concerns the thermal or catalytic pyrolysis at medium temperature to produce hydrocarbon rich liquids together with fuel gas [9]. Also in this case, the resulting bio-oils may contain high oxygen content and the presence of carboxylic acids may be a deep drawback [10,11]. A number of different catalysts have been tested for this reaction [9], such as protonic zeolites [12,13], acidic oxides [9,14], basic solid catalysts [2,15], redox oxides [16] and metal catalysts [17]. Mainly due to the complexity of the reaction and the possibility of leaching of the catalyst, still a clear picture of the reaction paths and mechanisms and on the best conditions to realize it are far from defined. In this paper we will focus on the presence of oxygenated compounds in the oils produced by pyrolysis of palm oil, on the role of catalysis and on the reaction paths. The catalysts have been used to convert palm oil in liquid/solid conditions, as well as to convert model molecules (acetic acid and ethyl acetate) in gas/solid conditions. This is done in order to have information on the role of catalyst functionality in the reaction path.

2. Experimental

2.1. Catalysts

The properties of the investigated catalysts are summarized in Table 1.

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Notation	Commercial name and composition	Manufacturer	Preparation	S_{BET}
MgO–Al$_2$O$_3$	Pural MG70 MgO:Al$_2$O$_3$ wt.%70:30	Sasol	Calcined at 773 K for 4 h	195
Al$_2$O$_3$	Puralox SBa 200	Sasol	From boehmite via Al alkoxides	190
SA1.5	Siralox 1.5/40	Sasol	As received	40
NaX	Sylobead MS C 544	Grace	As received	500
H-ZSM-5	CBV 5524G	Zeolyst	Calcined at 773 K for 4 h	425
H-USY	CBV 720	Zeolyst	As received	780

2.2. Catalyst characterization by infrared spectroscopy (IR)

Acidity measurements were done using the pure powders pressed into thin wafers and activated in the IR cell connected with a conventional outgassing/gas-manipulation apparatus at 773 K. The activated samples were contacted with pyridine vapor (p$_{Py}$ ~ 1 Torr) at room temperature for 15 min; after which the IR spectra of the surface species were collected in continuous evacuation at room temperature with increasing temperature.

2.3. Palm oil conversion experiments

The conversion of palm oil was performed in batch reactor (Fig. 1). Palm oil was loaded in the reactor without or with catalyst (3 wt.% vs
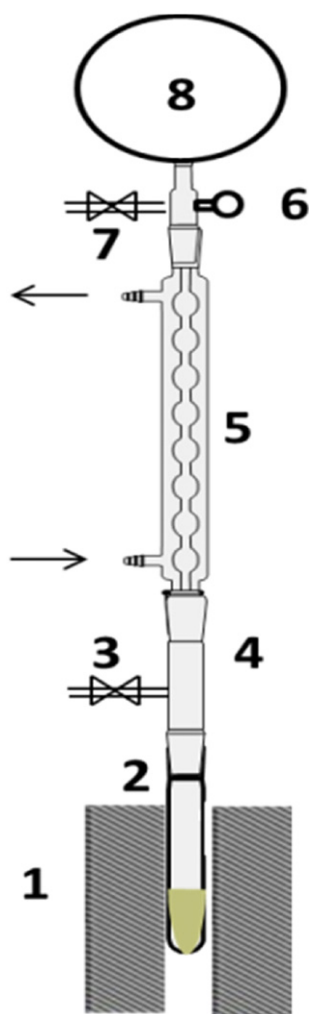
Fig. 1. Scheme of bench-scale catalytic pyrolysis reactor: 1) heater; 2) Pyrex glass reactor; 3) nitrogen gas inlet; 4) straight connecting adapter; 5) condenser; 6) silicon membrane; 7) nitrogen gas outlet; and 8) latex balloon.

oil mass). The temperature was raised to the desired value in 10 min by a controlled furnace, and then held for 2 h. Both input (palm oil) and output (unreacted palm oil in reaction products) materials were esterified by methanol to FAME (fatty acid methyl ester) in conditions where only triglycerides are (trans)esterified. The conversion of palm oil is calculated following equation:

$$X = \frac{(gFAME(palm\ oil) - gFAME(unreacted\ palm\ oil\ in\ products))}{gFAME(palm\ oil)}.$$

After the reaction, the gas phase was analyzed by FT-IR spectroscopy, GC and GC–MS while the residue was analyzed by FT-IR and GC–MS. In order to quantify, in the reaction residue, un-saponifiable and saponifiable (tri-, di- and mono-glycerides, esters and free fatty acids) fractions, saponification and separating processes were carried out in Pyrex glass round-bottom flask as follows: 100 mL of 2 N KOH in methanol was added into the reaction residue (1 g), and the mixture was shaken vigorously until it became free of dispersed fat particles. Saponification was conducted at room temperature overnight. A 100 mL portion of distilled water was added to the saponified mixture, which was transferred to Pyrex glass separating funnel with a Teflon stopper. Non-saponifiables were extracted three times, each time with 100 mL of diethyl ether. Pooled diethyl ether extracts were washed three times with 50 mL of 0.5 N KOH and 50 mL of distilled water, then that was vaporized in thermal static bath at 343 K overnight [18]. The extracted residue then was analyzed by FT-IR spectroscopy and GC–MS.

2.4. Catalytic gas phase experiments

Catalytic experiments were performed at atmospheric pressure in a tubular flow reactor (i.d. 6 mm) using 0.5 g catalyst (60–70 mesh sieved, to have a ratio between the particle diameter and the internal reactor diameter near 25) and feeding 2.1% v/v acetic acid (AA) in nitrogen with 0.49 h^{-1} WHSV (total flow rate of 80 cm^3/min), in the case of ethyl acetate (EA) feeding 12.5% v/v EA in nitrogen with 2.16 h^{-1} WHSV (total flow rate of 40 cm^3/min). The carrier gas (nitrogen) was passed through a bubbler containing acetic acid (99.9%, Carlo Erba) or

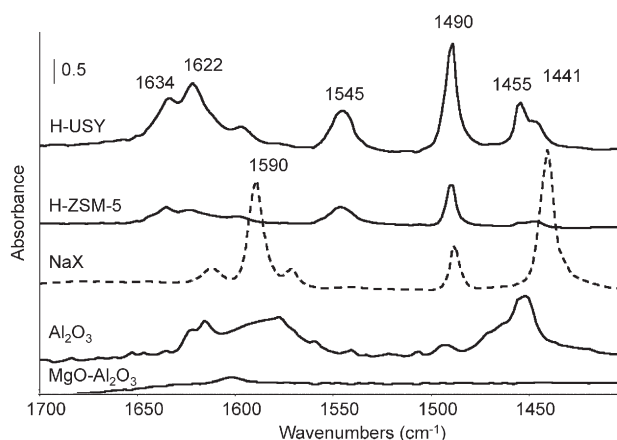**Fig. 2.** FT-IR subtraction spectra of surface species arising from pyridine adsorbed on investigated catalysts at 373 K.