Renewable Energy 60 (2013) 349–354

Contents lists available at SciVerse ScienceDirect

Renewable Energy

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

Technical note

Products and coke from the conversion of bio-oil acids, esters, aldehydes and ketones over equilibrium FCC catalysts

Melisa Bertero, Gabriela de la Puente, Ulises Sedran*

Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), (FIQ, UNL – CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

ARTICLE INFO

Article history:
Received 2 June 2011
Accepted 18 April 2013
Available online 10 June 2013

Keywords:
Bio-oil
Co-processing
FCC
Refinery

ABSTRACT

Reactivity and product distributions in the conversion of five different compounds representing typical species in bio-oils were studied over an equilibrium FCC catalyst at 500 °C during 60 s in a fixed bed reactor. Acetic acid, methyl acetate, furfural, 3-methyl-2-pentanone and 2-hidroxy-3-methylcyclopentenone were dissolved at 5% wt. in water. Thermal conversions were performed under the same conditions with inert SiC in the bed. The test compounds converted very differently, deoxygenation being produced by decarboxylation and dehydration. Furfural and 3-methyl-2-pentanone gave the highest yields of hydrocarbons, with high selectivity to light olefins and, when liquid (case of ketones), to aromatics. Methyl acetate gave the highest yield of oxygenated compounds. Coke yields were important (maximum 12.8% wt., 2-hidroxy-3-methylcyclopentenone). Thermal conversions were similar to the catalytic ones with acetic acid and methyl acetate, and much lower for the other reactants. Compared catalytic experiments, the thermal yields of hydrocarbons were much higher with acetic acid, and the yields of oxygenated higher with methyl acetate ester. Much less hydrocarbons were produced thermally with the other reactants. This information may be useful for predicting contributions if these compounds are to be co-processed in existing FCC units or upgraded over acidic catalysts.

1. Introduction

The liquid fraction from the pyrolysis of lignocellulosic biomass is usually referred to as bio-oil, and constitutes an alternative source for the production of fuels and raw materials for the chemical industry [1]. Bio-oils are complex aqueous mixtures of mostly oxygenated compounds, which have different chemical structures and a wide range of molecular weights; for example, bio-oils from different sawdusts contain mainly phenols, furanes, acids, esters, alcohols, aldehydes and ketones, with approximately 35–40% of oxygen, 55–60% of carbon, 15–60% of water, an acidic pH, and a density close to 1.2 g/cm^3 [2,3].

In order to transform bio-oils into transportation fuels, an upgrading process to remove oxygen could be performed with the help of catalytic cracking reactions over acidic zeolites, which mainly lead to hydrocarbons in the range of gasoline [3–7]. The conversion of oxygenated model compounds over zeolites and mesoporous materials showed that almost all of them formed hydrocarbons, the various functional groups indicating significantly different reactivities and product distributions [8–13].

Among the various options to upgrade bio-oils, their co-processing in existing industrial processes deserves special consideration, because by means of using present structure, no important process development and investments would be needed. Oil refineries, particularly the processes of thermal or catalytic cracking of hydrocarbons (FCC), might cover such an option, where bio-oils may play the role of non conventional feedstocks [14].

In the case of FCC, where the main component of the catalyst is the Y zeolite, the feasibility of adding bio-oils to the feedstock, which is usually vacuum gas oil, VGO, could be hampered by the high coke forming potential of bio-oils, which tend to polymerize at high temperatures [3–7]. Indeed, present day FCC technologies can handle heavy resid hydrocarbon mixtures, with Conradson Carbon Residue CCR higher than two, yielding more coke than conventional VGOs, by means of particular innovations such as catalyst coolers, two stage regeneration and more efficient strippers, among others [15,16]. In order to facilitate co-processing in FCC, the previous thermal treatment of bio-oils induces important changes in their composition, with reductions between 30 and 50% in the amount of phenols [17], which are assumed to be main coke precursors; as a consequence, up to 30% decrease in the yield of coke was observed with previously treated bio-oils [7,18]. Other possible drawback in the approach is the significant content of water in bio-

* Corresponding author.
E-mail address: usedran@fiq.unl.edu.ar (U. Sedran).

0960-1481/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.renene.2013.04.017

oil and the fact that it may be not possible to dissolve it into VGO; some options were discussed by Corma et al. [19].

The study of the reactivity of bio-oil model compounds representing different chemical functionalities over actual, equilibrated commercial FCC catalysts, as well as of the product distributions observed, could provide useful information to predict co-processing details. Particularly, the chemical groups which are responsible of higher coke yields, or which show more efficiency in being converted into hydrocarbons, could be identified. At present that information is scarce. It is the objective of this work to study the conversions and product selectivities of acids, esters, aldehydes and ketones, in terms of model compounds, on an equilibrated commercial FCC catalyst, and compare them with the same observations on an inert material used to represent thermal cracking reactions.

2. Experimental

The model compounds (Sigma–Aldrich) used were acetic acid (99.8%, named ACET), methyl acetate (99.5%, MACET), furfural (99%, FUR), 3-methyl-2-pentanone (99%, MP) and 2-hidroxy-3-methylcyclopentenone (98%, HMCP), to represent acids, esters, aldehydes and linear and cyclic ketones, respectively. Each of the reactants was dissolved in water with a concentration of 5% wt, as an approximation to the conditions observed for the respective chemical groups in typical bio-oils from conventional pyrolysis processes.

The equilibrium FCC catalyst used (E-Cat) was of the octane-barrel type, sampled from a running refinery, its most important characteristics being shown in Table 1.

The conversion experiments were performed in a stainless steel MAT (ASTM D-3907/03)-type fixed-bed reactor of 15.6 mm diameter and 400 mm length, which has a porous metal plate in its mid position to support the 2 g catalyst bed. The reactor was heated in an electrical furnace up to the reaction temperature of 500 °C under nitrogen flow of 30 mL/min. The reactants were fed by means of a SAGE Instruments Model 3414 pump, with flows of 0.7 mL/min. Reactor effluents were passed through an ice-water condenser where most of the liquids were retained, and gases were collected and quantified by displacement of water in a glass column. In all the cases the time on stream was 60 s, after which a sweeping flow of 30 mL/min of nitrogen was passed during 7 min. Mass and carbon balances (recoveries) were higher than 90% in all the cases. Thermal cracking reactions were performed under the same conditions with a bed of inert SiC occupying the same volume as the catalytic bed.

Liquid and gas products were analyzed by conventional capillary gas chromatography in an Agilent 6890N gas chromatograph equipped with a 30 m length, 0.25 mm i.d. and 0.25 μm phase thickness HP-1 column and FID detection. Gases were also analyzed with a 30 m length, 0.53 mm i.d. and 3.0 μm phase thickness GS-CARBONPLOT column and TCD detection. Products were identified by means of the use of standards and the GC–MS technique. The calibration of the chromatographic areas was performed by using response factors for each of the chemical groups, assessed from mixtures of standards and a reference compound (tetralin for liquids and methane for gases). Unidentified peaks, each representing less than 0.5% of the total chromatographic area were assigned an average response factor.

The amount of water in the liquid products was determined by means of the Karl-Fischer method (IRAM 21320). The amount of coke on the reactor bed was assessed with a combined method of thermal programmed oxidation (initial temperature, 250 °C during 15 min; heating ramp, 16 °C/min; final temperature, 700 °C, during 16 min) and further conversion of the carbon oxides formed to methane on a Ni catalyst, which was quantified with a FID detector. The various product yields were calculated as the relationship between the corresponding mass of product and the mass of reactant; water yield was assessed by difference from the mass balance.

Table 1
Properties of the catalyst E-Cat.

Particle size (μm)	100–120
UCS (Å)	24.26
Zeolite load (%)	18.0
Specific surface area (m^2/g)	158.0
t-Plot micropore volume (cm^3/g)	0.046
Fe (%wt.)	0.35
Ni (%wt.)	0.06

3. Results and discussion

The model compounds were selected based on the composition of bio-oil derived from the conventional pyrolysis of pine sawdust [17], selecting compounds that represent some of the most important chemical groups, such as acids and esters (typically present at about 30% wt.) [20], aldehydes and ketones (with typical concentrations from to 2 to 20% wt. and about 7% wt., respectively [20]). Moreover, some of the compounds, such as FUR and HMCP, were the most important in the group they represent.

In their conversion on acidic zeolites, acids, esters, aldehydes and ketones react through a mechanism involving decarbonylation, decarboxylation, dehydration, cracking and aromatization, thus yielding mainly aromatic and aliphatic hydrocarbons and oxygenated compounds covering a wide range of molecular weights [9,10,13,21–23].

In all the cases liquid, gases and solid (coke) products were generated by the catalytic and thermal conversions of the model compounds. The amount of water in the liquid stream represented from 96 to 99% of the liquid fraction, accounting for solvent water and product water from dehydration reactions. Table 2 shows the conversions and the yields of the different product groups, where significant differences can be observed among the five reactants. Most noticeable facts on E-Cat are that under the conditions used the highest conversion and yield of oxygenated product corresponded to MACET (95.1%), while MP and FUR yielded much more hydrocarbons than the other reactants, selectivities being 47% and 41%, respectively. The highest producer of oxygenated compounds was MACET, and HMCP yielded the highest amount of hydrogen (8.1% wt.) and carbon dioxide (35.7% wt). Maximum dehydration was observed with FUR (12.8% wt.).

The published literature about the conversion of these model compounds, or similar, on FCC catalysts or Y zeolite, which is their main component, is very scarce. For example, Hutchings et al. [8]

Table 2
Thermal and catalytic conversions and product yields from the model compounds. Temperature: 500 °C.

	ACET		MACET		FUR		MP		HMCP	
	SiC	E-Cat	SiC	E-Cat	SiC	E-Cat	SiC	E-Cat	SiC	E-Cat
Conversion (%)	45.0	50.4	95.3	95.1	21.6	78.2	24.9	79.6	37.7	84.5
Yields (%wt.)										
Hydrocarbons	10.4	4.2	0.4	0.9	5.3	32.1	0.3	37.6	5.0	14.0
Oxygenated	5.0	5.2	81.6	54.5	0.7	9.0	17.9	20.7	14.4	9.4
Hydrogen	17.5	6.6	5.2	3.7	6.7	5.7	0.6	0.5	3.7	8.1
CO_2	8.2	22.9	3.0	22.2	1.1	9.6	1.2	1.1	1.9	35.7
CO						1.8				1.2
Water	3.6	9.9	4.7	6.4	6.8	12.8	3.1	13.7	10.0	2.3
Coke	0.3	1.6	0.4	7.4	1.0	7.2	0.1	5.9	0.7	12.8
Unknown							1.7		2.0	1.0