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Hydrotreatment of pyrolysis oils from biomass: reactivity of the various categories of oxygenated compounds and preliminary techno-economical study

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Abstract

This paper describes essential aspects of the hydrotreatment of pyrolytic oils in the light of results obtained until now at the Université Catholique de Louvain. Stability of pyrolysis oils necessitates a two-step processing. A low temperature hydrotreatment enables stabilization through reactions like olefin, carbonyl and carboxylic groups reduction. Further hydrotreatment aims at hydrodeoxygenation of phenols and hydrocracking of larger molecules. Results about catalysts, reaction conditions and parameters enabling or influencing the control of the reaction are summarized. Based on these laboratory data, a preliminary techno-economical evaluation is made. 50 wt.-% yields in hydrocarbons for deep hydrorefining of pyrolysis oils can be expected. Nevertheless, a moderate hydroconversion with partial elimination of oxygen would be, economically, more advantageous.

Keywords: Hydrotreatment of pyrolysis oils

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1. Introduction

The pyrolysis of biomass to produce gases, tars, aqueous organic condensates (pyroligneous acids) and chars has been known since the earliest stages of human technologies [1]. For many centuries, the emphasis has been laid on the production of gases and chars that were used respectively as a source of chemicals and domestic and industrial combustibles [2]. Since the last oil crisis, interest in pyrolysis has been centred on liquid production [3]. These liquids, called bio-oils or bio-crudes, combine many advantages: easier handling and transport, high energy density and flexibility of use compared to raw biomass and other pyrolysis products, low nitrogen and sulfur content compared to petroleum products [4].

Methods related to the flash pyrolysis [5–8] allow to obtain high liquid yields with a high heating rate and short reaction time. Among flash pyrolysis processes, rapid thermal processing (RTP) is a particular heat transfer process operating at extremely short residence times with an intense thermal action. A rapid quenching preserves initial valuable depolymerization products [9,10].

Flash pyrolysis oils and all bio-oils are intended to be used in direct combustion in boilers or gas turbines. Nevertheless, it is generally

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agreed that many improvements are necessary to overcome unwanted characteristics of these oils. In fact, with an oxygen content close to 40%, they contain mostly oxygenated functions that are the origin of a bad thermal stability, a poor heating value, a low volatility and some corrosivity. The elimination of oxygenated functions is the easiest way to upgrade pyrolysis oils [11]. Two methods are proposed: deoxygenation without reducing gases over zeolitic catalysts [12] and high temperature hydrotreating in the presence of a catalyst similar to those used in petroleum hydrotreating processes [13,14]. A quite extensive determination of the chemical composition and the physico-chemical properties of the oils is crucial for the development of these upgrading processes [15].

This paper is a review of the main results obtained in our laboratory concerning the reactivity of the various categories of oxygenated compounds and the parameters influencing the hydrodeoxygenation reactions. In addition, we present a first assessment of the feasibility of this process and a preliminary economic study.

2. The hydrodeoxygenation process

2.1. Model compounds reactivity

The primary objective of the research was to demonstrate the performance of sulfided catalyst for the deoxygenation of all the chemical groups present in pyrolysis oils and to get information optimizing the reactions. Because of the high instability of pyrolysis oils when heated at temperatures of about 350–400°C, which are typically those used in hydrotreatment, an extensive degradation may take place and the oil could become a very hard, coke-like, material. Generally, this chemical instability is attributed to unsaturated double bonds (olefins, aldehydes, ketones) which may react through condensation reactions similar to the phenol–formol polymerisation (as for the synthesis of bakelite). It is, thus, highly desirable to eliminate these functions as quickly as possible before they react to high molecular weight compounds. Experiments with oxygenated model compounds show that this can be accomplished by a low temperature hydrotreatment. This is shown in Table 1 where the reactivities of oxygenated model compounds in presence of a commercial Co–Mo hydrotreating catalyst are presented. The reactivities are reported as the temperatures at which the conversion rates reach a significant identical value. The same oxygenated chemical groups in pyrolytic oils will be eliminated at similar temperatures. The hydrogenation of the carbonyl group of 4-methyl acetophenone is performed at a temperature of 100 to 200°C lower than the temperature needed for the elimination of methoxyl, phenolic or furanic oxygens. The carboxylic ester group has an intermediate reactivity. We may estimate that unsaturated double bonds (olefins), aliphatic alcohols and ethers will react at even lower temperature than the ketonic group. Consequently, a low temperature hydrotreatment would enable the stabilisation of pyrolysis oils which would then show better properties for storage or transport and could be used in normal heavy fuel utilizations or for

Table 1
Influence of the temperature and hydrogen consumption

	Activation energy (Kcal/mol)	Temperature of iso-reactivity (°C)	Hydrogen consumption
Ketone	12	203	$2H_2$/function
Carboxylic	26	283	$3H_2$/function
Methoxy phenol	27	301	up to $6H_2$/molecule
4-Me phenol	33.6	340	up to $4H_2$/molecule
2-Et phenol	35.8	367	up to $4H_2$/molecule
Dibenzofuran	34.1	417	up to $8H_2$/molecule

phenols recovery. A full hydrorefining of pyrolytic oils would require a temperature comprised between 350 and 425°C for the elimination of the phenolic and furanic oxygens and the conversion of the heavy molecules. Conducted in more severe conditions with the prestabilized oil, the treatment would enable total oxygen elimination and recovery of a high grade hydrocarbon product comparable to those obtained from petroleum. The hydrogen consumed by the elimination of various chemical groups shows an evolution parallel to the severity required. As the unsaturated bonds (olefin, aldehyde, ketone) are easily hydrogenated, the hydrogen addition is relatively specific. In contrast, the reactions taking place at higher temperature are less specific and a high quantity of hydrogen is consumed by the hydrogenation of adjacent aromatic rings.

2.2. Parameters influencing or enabling a control of the hydrodeoxygenation reaction

Besides the influence of temperature, other parameters inherent to the composition of pyrolysis oils (H_2O, N-compounds) or vital for the functioning of hydrotreatment catalysts (H_2S) were studied. Results were presented in former meetings [11] and will be summarized in this paper.

2.2.1. Water

Water has very little influence on the deoxygenation reactions. Although present in large amounts in the batch reactor, the deoxygenation rates are practically unchanged. This is interpreted as resulting from a low adsorptivity of H_2O on the sulfided phases responsible for the reactions.

2.2.2. NH_3

Ammonia is representative of nitrogen compounds present in bio-oils in quantities depending on the origin of the pyrolyzed biomass. It has an inhibiting action on nearly all the hydrodeoxygenation reactions. The inhibition, due to blocking of active sites, is at least one order of magnitude higher than the inhibition by oxygenated compounds or H_2S. This indicates that the nitrogen content of pyrolysis oils, although generally low, cannot be neglected. The deoxygenation of carbonyl groups is surprisingly not affected by ammonia, in contrast to all other reactions.

2.2.3. H_2S

Hydrogen sulfide is known to be an important parameter for the stability of sulfided catalysts. We also observed this parameter to be important for the control of the activity and selectivity. H_2S, especially, strongly influences the hydrogenation–hydrogenolysis selectivities in the conversion of phenols. H_2S promotes certain reactions such as the decarboxylation of carboxylic groups. The partial pressure of H_2S is a parameter for the control of hydrogen consumption.

3. Preliminary techno-economical study

3.1. The hydrotreating of the real oils

The feasibility of the hydrotreating of biomass-derived oils has been demonstrated at the laboratory scale by several authors these last ten years [13–15]. Table 2 compares the requirements for hydrotreating biomass pyrolytic oils (simple stabilisation or full refining) with the conditions used for many decennia in the hydrotreating of petroleum fractions (hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrocracking (HCK)). It is clear that the similitudes are so large that the HDO of pyrolytic oils will be just another extension of the same technology. This will probably be easier to develop than the refining of the heavy crudes which presently correspond to a very large proportion of the feed of refiners, and this will be much easier than to obtain sulfur free transportation fuels on which refiners are working presently.

Hydrogen has consistently been a problem when projects on pyrolytic oil hydrotreating were introduced. Table 2 shows that the hydrogen consumption per ton is quite comparable to that in the petroleum industry. It is even smaller than that for difficult feeds in hydrocracking. As, in spite of the high hydrogen consumption, these hydrocracking processes are profitable, this shows that the amount of hydrogen required is not a real problem.

Another objection dealt with the size of the necessary hydrogen producing plant. Much progress is made presently on constructing smaller hydrogen units thanks to new technologies. Table 3 lists some of them. The capacities of these small pilot plants should be compared to the volume of hydrogen required by a 10000 t/year bio-oil refining plant. These are, according to our former figures, 10000 Nm^3/day and 22000 Nm^3/day for a stabilisation and full refining treatment, respectively. This correspond roughly to presently available technologies.

In Table 4, the energetic potentials that the development of an efficient route from biomass into useful energy may offer are presented. The figures are the potential production for the EC (year 2000) [16] and prices of various biomass-derived fuel in ECU per ton equivalent-oil (namely for equal heat content). The potential raw biomass production of EC is calculated from the projections of Grassi and Bridgwater [16] for the year 2000. For ethanol and rapeseed oil esters, the basis is agricultural land laying waste by the EC policy (this correspond to a potential of 500 Mt dry matter of biomass mentioned in Grassi and Bridgwater's report). For stabilized or refined oil, this corresponds to, in addition, marginal land and agricultural residue

Table 2
Comparison of the requirements and conditions of the hydrotreating of pyrolytic oils and petroleum fractions

	Pyrolytic oils HDO	Petroleum refining HDS, HDN, HCK
Equipment, plant	← same →	
Pressure	← same: 30–100 bars →	
Catalysts	← same type; Co, Ni, Mo (sulfided) →	
Size	Desired = ca. 10000 t/y	in operation 5000 → 1 000 000 t/year
H_2 consumption Nm^3/t	340–730	200–800
Analytical technique	← same methodology →	

Table 3
Capacity and economics of new small scale hydrogen production plants

	Feed	capacity Nm^3/day	cost ECU/Nm^3	Ref.
Haldor Topsøe	methanol	1200–47500	–	[13,14]
Tokyo Gas Co.	CH_4 (town gas)	–	0.45	[15]
Johnson Matthey PLC (Hot Spot Reactor)	LPG oil (or methanol)	(pilot) 30	–	[16–19]

Table 4
Potential for production and prices of various biomass derived liquid fuels (Ref. [17–21])

	t (dry)/ha	energy GJ/t	toe/ha	price ECU/toe	EEC potential Mtoe/year
ethanol	5–6	26.8	3.3–4.0	530	92
ester (rapeseed)	1.2–1.6	37.7	1.13–1.51	400–440	33
refined oil	7.5–12.5	40	7.5–12.5	335	≅ 245
stabilized oil	11.5–17.5	28	8–12.2	260	≅ 280
lead-free gasoline (extra)				230	

ha, hectare; toe, ton equivalent; Mtoe, million ton equivalent.

(890 Mt dry matter). For comparison, let us note that the total refining capacity of Western Europe (EC + the Nordic countries + Switzerland + Austria) is about 630 Mt mineral oil/year. EC crude oil consumption is about 490 Mt/year of which 150 Mt is produced in Europe [16]. Liquid products derived from pyrolysis oil would correspond to a very substantial percentage of petroleum derived fuels used yearly in Western Europe. In principle, Europe could cover half of its liquid fuel consumption with oils derived from bio-oil.

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