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Coke chemistry under vacuum gasoil/bio-oil FCC co-processing conditions

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ABSTRACT

This study presents an in depth investigation of the coke chemistry occurring in FCC and USY catalysts during co-processing of fossil feeds (VGO type) blended with various types of upgraded bio-oils produced by fast pyrolysis of lignocellulosic bio-mass. It includes a brief survey of previous studies devoted to the effect of co-processing on FCC products yield and quality. A combination of two main processes is proposed to account for the marked increase in coke formation in the presence of oxygenated molecules in the reacting feed: (i) the conventional cracking route for the VGO fossil hydrocarbons leading to essentially graphitic coke deposited preferentially in the USY zeolite micropores, and (ii) the conversion of lignin fragments into hydrocarbons, residual light oxygenates (essentially phenolic type) and finally "bio-coke" which accumulates in mesopores as less structured coke as compared to the harder coke issued from hydrocarbons condensation. These two routes which are monitored by the catalysts structure, texture and acidity are strongly interacting via hydrogen transfer between light hydrocarbons and phenolic type fragments. A tentative mechanistic scheme is proposed.

1. Introduction

In order to meet the international binding renewable energy targets by 2020 (10% share in all forms of transportation fuels) without competing with the food value chain [1], a realistic alternative to the first generation of bio-fuels is to produce second generation hybrid bio/fossil fuels by co-refining non edible biomass pyrolysis oil with crude oil fractions in a conventional oil refinery [2–5], as recently reviewed by Graça et al. [6]. This approach aims at co-processing bio-oils in HDT or FCC units without modifying their routine operations, which would reduce both cost and risks. However, previous researches carried out in our laboratory have shown that co-refining may lead to significant changes in products quality, especially for the case of FCC process with mainly (i) higher liquid products aromaticity and (ii) larger coke deposits [7]. For the former, higher content of aromatics combined with higher liquid products yield might be beneficial under coprocessing conditions if the FCC operator is targeting more LCO (diesel fraction) than gasoline. For the later, it is well known that the amount of coke depositing on spent FCC catalyst affects the heat balance of the system since coke burning is the source of heat used for the endothermic cracking reaction and feed vaporization in the FCC reactor. Thus, mathematical simulation, as reported for example in [8], shows that for 1 wt.% of coke deposit, the heat produced from the burning reaction is not large enough to maintain the reaction, ending with carbon remaining on the regenerated catalyst. In turn, too high coke contents, which might be the case under co-processing conditions, will overheat the regenerated catalyst and cause hydrothermal processes that deactivate the catalyst permanently. Therefore, this potential issue on coke formation generated by the addition of bio-oil in the FCC feedstock has to be carefully considered in the co-processing operation. It can be noted however that other operating parameters could be adjusted to deal with a higher amount of carbon content in the spent catalyst such as higher gas space velocity in the regenerator to remove the heat excess generated by coke burning. Similarly, potential changes in the coke nature (density, graphitization, hydrogen and/or oxygen content) and location under co-processing conditions might also be parameters to consider during the regeneration process.

The present study will focus on these specific aspects of the co-processing, carried out at lab-scale in a MAT (Micro Activity Test) type reactor, scarcely reported specifically in the literature [30]. First, the main impacts of co-processing on liquid products quality and coke formation will be surveyed from data already published

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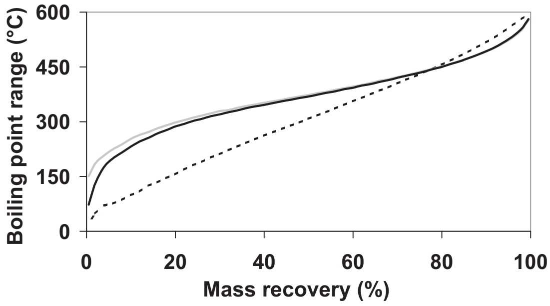

Fig. 1. Boiling point distribution as a function of mass recovery of the starting materials (HDO-oil: –, VGO: ▬ , VGO/HDO-oil mixture: ▬).

by our group. Then, the main trends observed under processing (conventional VGO feedstock) and co-processing (VGO or long residue blended with upgraded bio-oils) conditions on coke formation, nature and location together with its ability to be oxidized under temperature programmed oxidation (TPO) conditions will be reported, as original data. The used up-graded bio-oils are either obtained by hydrodeoxygenation of fast thermal pyrolysis oil produced from wood-based bio-mass (named HDO) or are produced by catalytic fast pyrolysis of wood-based bio-mass (named CPO) [14], eventually followed by a thermal conditioning for decreasing the coke formation during downstream FCC [9]. It is noteworthy that the results of that MAT scale study will not directly reflect the effective coke chemistry occurring in real industrial FCC units. However, the general trends reported either for coke composition and nature or for its formation mechanism can serve as guidelines for better understanding of more realistic data collected at pilot scale level, without even considering data collected at industrial scale where the sampling of spent catalysts is already a technical challenge in itself [21].

2. Experimental

2.1. Feedstocks and catalysts

All the used feedstocks, catalysts, MAT reactor and on- and off-line reactants and products analyses are described in details in [7,14]. Various crude oil distillates as vacuum gas oil (VGO) and upgraded bio-oils as hydrotreated thermal pyrolysis oil (HDO) or catalytic pyrolysis oil (CPO) were used to check the impact of the nature of the fossil and of the bio feedstocks on the co-processing chemistry, respectively. Typically, boiling temperature distributions of typical feeds as VGO, CPO or a mixture VGO/CPO obtained from SIMDIS analysis are reported in Fig. 1.

As can be seen, the first 20 wt.% of the VGO sample is in the range of 150–300 °C while the HDO-oil is in the range of 40–150 °C. This difference is reflected in the SIMDIS plot of the VGO/HDO-oil mixture where the first 20 wt.% of the sample correspond to the 70–270 °C boiling point range. However, the trend of the boiling point curve of the VGO/HDO mixture is comparable to that of the pure VGO one. Similar trends are observed for VGO/CPO mixtures.

Elemental compositions of a representative series of VGO, HDO and CPO feedstocks, used throughout the study unless otherwise specified, are reported in Table 1.

Table 1
Density and elemental analysis of the main feedstocks used in the present study.

Density and nominal composition	VGO	HDO	CPO
Density (g/cm^3 at 25 °C)	0.8953	0.9323	–
Carbon (wt.%)	85.4	69	66
Hydrogen (wt.%)	12.4	10	7
Oxygen (wt.%)	–	21	27
Nitrogen (wt.%)	0.07	–	<0.10
Sulfur (wt.%)	2.02	–	<0.20
H_2O (wt.%)	–	3	11

Table 2
Typical compounds of bio-oils fractions used for co-processing [11].

	Compounds	Concentration (wt.%)
Acids	Acetic acid	3.33
	Formic acid	0.56
		0.18
Aldehydes	Glycolaldehyde	1.57
	3-Hydroxypropionaldehyde	0.06
Sugars	Levoglucosan	1.07
	Dianhydroglucopyranose	0.06
	Xylanose	0.02
Ketones	Acetol	0.48
	Cyclopentenones	0.15
	1-Hydroxybutan-2-one	0.05
	Acetoxyacetone	0.02
	Butadiene	0.02
Phenolics	Syringols	0.23
	Guaiacols	0.13
	Phenols	0.01
Furans	Furanone	0.21
	1,4-Lactone	0.02

Indeed, the composition of the co-processed pyrolytic oils strongly depends on the various up-grading steps implemented after the initial fast pyrolysis of bio-mass resources (pine wood for the present case). The starting material can be considered as a complex mixture of water (15–30 wt.%) and a large number of compounds (approx. 300), including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, phenolics (phenols, guaiacols, catechols, syringols, eugenols) and other oligomeric lignin derivatives. In general, water addition to the raw oil allows to split it into an aqueous and an oil (organic) phase enriched in polar and non-polar compounds, respectively. The former is alternatively hydrodeoxygenated to decrease its oxygen content, and make it more miscible with crude oil distillates, as well described in [10]. Concerning the molecular composition of theses up-graded bio-oils, despite use of advanced analytical techniques (including HPLC/MS and GC–GC/MS), most chemicals are lumped into distinct families. The concentration of typical compounds identified in HDO phases is given in Table 2.

Note that the lignin derivatives which form the majority of the heavy fraction to be cracked under FCC conditions are not included in the list, being too heavy to be analyzed by conventional chromatography. However, they are revealed by adapted techniques such as gel permeation chromatography (GPC), as shown in Fig. 2. Here it can be seen that the larger fraction of material with molar weights over 800 g/mol corresponds to lignin fragments.

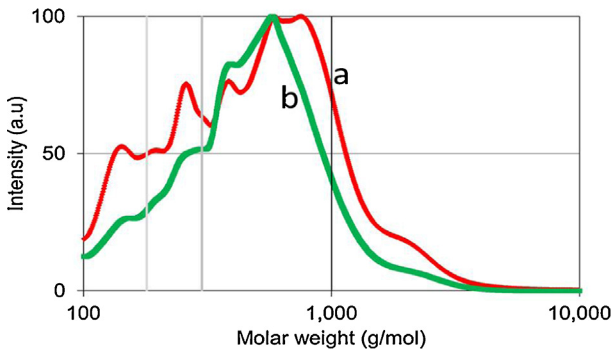

Fig. 2. GPC profile of the two types of bio-oils used in the present work: a, CPO; b, HDO.