

## Process-product studies on pyrolysis oil upgrading by hydrotreatment with Ru/C catalysts

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### Introduction

Biomass is considered an attractive alternative source for fossil derived energy carriers, liquid transportation fuels and bulk-chemicals [1]. Liquid energy carriers can be obtained by biomass liquefaction followed by further upgrading. A promising liquefaction approach is fast pyrolysis [2]. The product, pyrolysis oil, is a viscous liquid, with a high oxygen content (up to 40 wt%). The latter renders the oil polar and acidic due to the presence of organic acids. Various upgrading technologies have been proposed to improve the product properties to extend the application range. An attractive approach to extend the application range of pyrolysis oil is by its co-feeding into existing refineries, either in hydrotreating or FCC units. However, pyrolysis oil as such is not directly suitable for this purpose, because the oil is not miscible with hydrocarbon feedstocks and, moreover, shows a high tendency for coking, leading to blockage of feeding lines and reactors.

A promising upgrading technique is catalytic hydrotreating using hydrogen in combination with heterogeneous catalysts [3]. Typically, the objective is to obtain upgraded oils with very low residual oxygen contents to mimic the conventional crude oils. A major drawback of this approach is the high hydrogen consumption, which has a strong negative impact on the process economics [4].

An alternative is a mild hydrotreating process at a much lower severity than the conventional hydrotreating processes. Here we report experimental studies on the hydrotreating of pyrolysis oil at different severities in bench scale continuous packed bed reactors, addressing oxygen content, water content, average molecular weight and the tendency of coking of the products obtained.

### Experiment Section

#### Materials

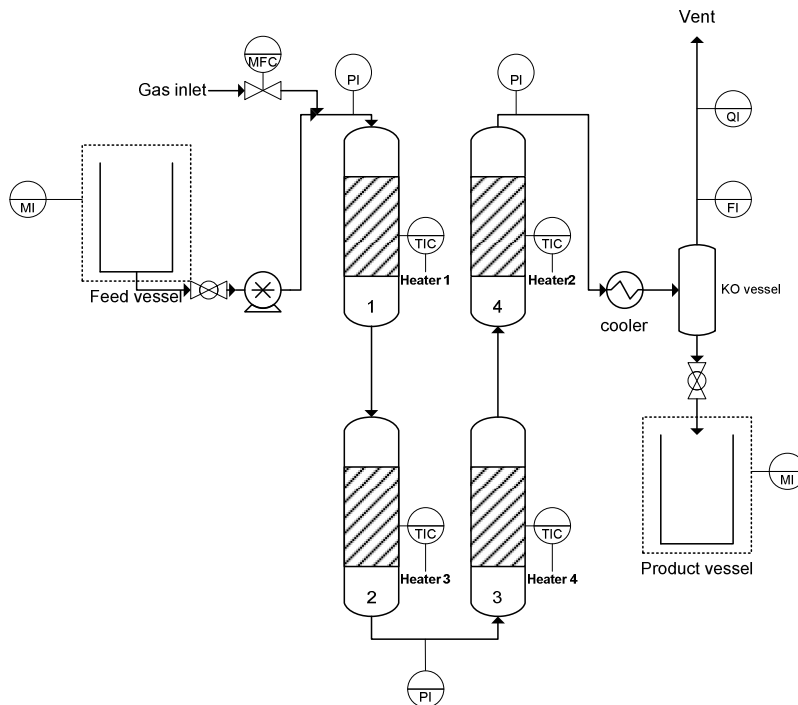
Pyrolysis oil was obtained by fast pyrolysis of forest residue and the composition is given in Table 1. Ru/C was used as the hydrotreating catalyst (5 wt% Ru, pelletized). The hydrogen used was of 99.9% purity.

**Table 1.** Elemental composition of the pyrolysis oil used in this study

Elements	Composition (weight %)
C	40.1
H	7.6
N	0.1
O (by difference)	52.1
O (dry basis)	40.1
Water	23.9

## Reactor set-up

A schematic representation of the set-up used is given in Figure 1. The main part of the set-up is four tubular reactors-in-series filled with catalyst. The temperature of each reactor can be controlled independently.



**Figure 1** Experimental set-up used for pyrolysis oil hydrotreatment

## Typical description of a hydrogenation experiment

Pyrolysis oil was pumped through the reactors. After stable liquid flow was obtained the hydrogen was fed into the reactor, then the pressure and temperature were raised to the desired conditions (200 bar of hydrogen pressure, other details see Table 1). The products (gas and liquid) were separated in a knock out vessel. The gas was vented and the liquid was collected in bottles. The temperature, pressure, flow of gas and liquid in and out of the reactors were recorded.

## Results and discussion

The experimental studies were carried out in a bench scale continuous set-up with four packed bed reactors in series (Figure 1). The temperature in each reactor is independently set at the pre-determined values. Ru/C was used as the catalysts and a fixed hydrogen pressure of 200 bar was applied. The pyrolysis oil feed rate and the temperatures were varied, see Table 1 for details.

**Table 1** Experimental conditions

Code	Temperature (°C) <sup>a</sup>	WHSV (hr <sup>-1</sup> )	Process	Oxygen content (wt%, dry)
Py-oil				40.1
1	175-175-175-175	7.13	stabilization	35.4
2	225-225-225-225	7.11	stabilization	27.8

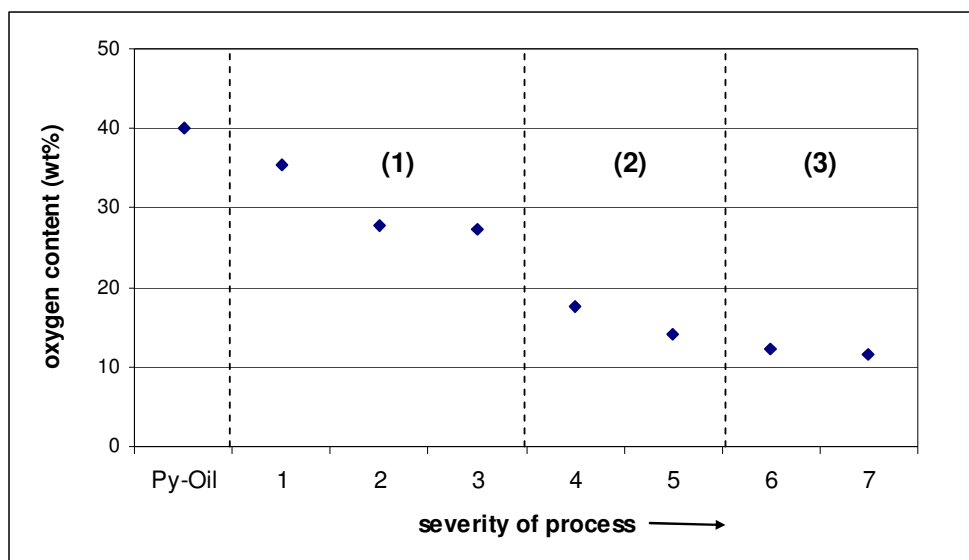
3	275-275-275-275	11.17	stabilization	27.4
4	175-225-300-350	5.57	Mild hydrotreating	17.6
5	175-275-375-400	1.23	Mild hydrotreating	14.2
6	350-375-400-400	2.51	2-stage hydrotreating	12.3
7	350-375-400-400	2.35	2-stage hydrotreating	11.5

<sup>a</sup>temperature profile along 4 packed-bed reactors

For all experiments except run 1 two liquid products were obtained, viz. an aqueous phase and brown-red organic phase. The elemental composition, water content and average molecular weight of the organic product were determined. To gain insights in the coking tendency of the products, the samples were analyzed using TGA. The residual-weight at the end of the TGA scan was taken as a measure of coking, with a high residue indicating a high tendency for coking.

The oxygen content of the organic phase as a function of the process conditions is given in Figure 2, where the oxygen content of the product oil (dry basis) is depicted versus the severity of the experiments (higher severity means higher temperature and/or lower WHSV). Higher severity leads to lower oxygen contents. At low temperatures (175-275°C, stabilization step), the oxygen content reduces from 40.1% to 27.4 wt%.

A number of experiments were carried out at different temperatures for the 4 reactors (code 4-5). The first reactor in the set-up was set at 175°C, the last either at 350 or 400°C. At these conditions (mild hydrotreating), the oxygen content was reduced to about 14.2 wt%.



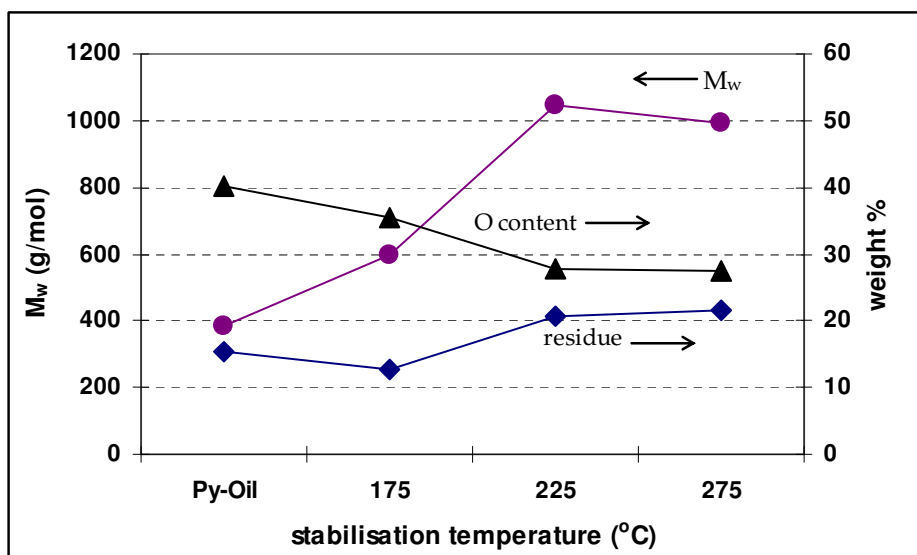
**Figure 2** Oxygen content as function of process severity, (1) stabilization, (2) mild hydrotreating, and (3) 2-stage hydrotreating.

The product oil obtained at mild hydrotreating conditions (code 4, Table 1) was subjected to a second hydrotreating procedure at high temperatures (350-400°C, see code 6 and 7 in Table 1, 2-stage hydrotreating) as the oil was already stabilized. Also again two phases

formed, viz. a black oil phase floating on top of a clear water layer. The oxygen content of the oil was reduced to 11.5 wt% at a WHSV of 2.35 h<sup>-1</sup>.

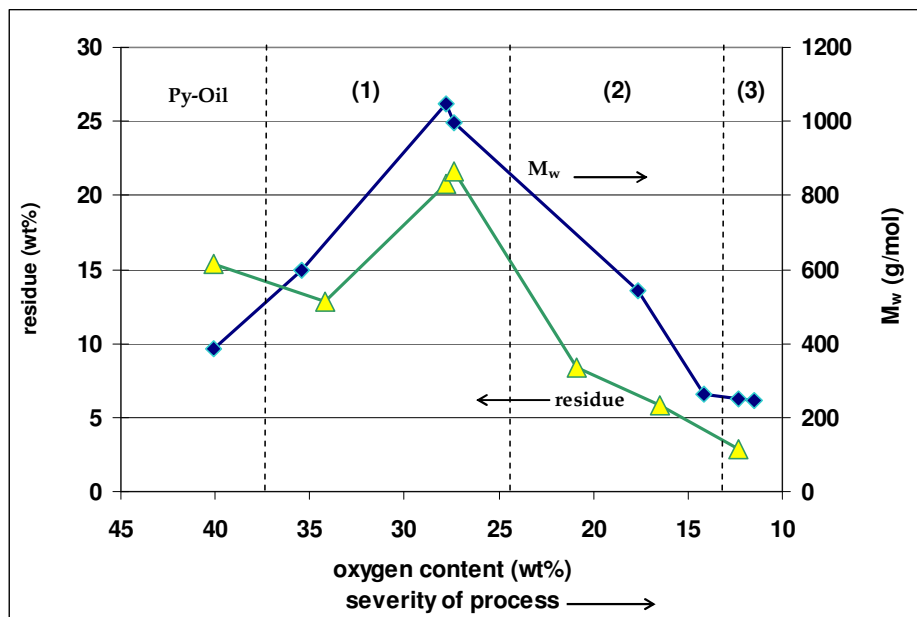
The products of the stabilization steps (code 1-3, Table 1) were analyzed by GPC and TGA and the results are given in Figure 2. The molecular weight of the product increases upon going from 175°C to 275°C. Apparently, polymerization occurs during the stabilization step. This phenomenon has also been observed when heating up pyrolysis oil to 275°C in the absence of catalysts (HTTP process) [5]. The oxygen content of the product decreases, thus also hydrogenation occurs to some extent.

The residue after a TGA measurement is also a strong function of the temperature in the stabilization step. The residue is considerably higher at 275°C, and consequently has a higher tendency for coking and may be less suitable as a refinery feedstock. Of particular interest is the relation between the molecular weight of the products and the TGA residue. Products with a higher M<sub>w</sub> also give higher TGA residues. This may be rationalized by assuming that the higher molecular weight fragments in the products are precursors for coke formation.



**Figure 1** Oxygen content, mass average molecular weight and residual weight of organic phases obtained at 175-225°C (run 1-3 in Table 1).

The molecular weight and the TGA residue were also measured for the other samples in the series and the results are given in Figure 2. In this case, the oxygen content is taken as the independent variable, being an indicator for the severity of the process. For clarity, the results of the stabilization step are also provided.



**Figure 2** Mass average molecular weight and TGA residue of products from (1) stabilization, (2) mild hydrotreating, and (3) 2-stage hydrotreating.

The molecular weight of the products obtained at mild hydrotreating conditions (code 4-5, Table 1) are considerably lower than those produced in the stabilization phase (code 1-3). This suggests that the rate of molecular weight breakdown by hydrogenation or cracking reactions was on average much higher than the rate of polymerization. The TGA residue was also reduced considerably and again showed a clear relation with the molecular weight. The molecular breakdown continues during the 2-stage hydrotreating, resulting in organic products with even lower molecular weights and TGA residual weights than observed for product from the mild hydrotreatment procedure.

### Conclusions and outlook

Hydrotreatment of pyrolysis oil at different severities in bench scale continuous packed bed reactors were performed. At temperature higher than 175 °C the liquid product separated into an aqueous and organic phase. The oxygen content of the organic phase reduced proportionally with the severity.

During the stabilization experiments, polymerization (represented by increase of molecular weight) occurs faster than hydrogenation (represented by deoxygenation). Stabilization alone therefore appears not sufficient to make suitable product for refinery co-feeding.

During mild hydrotreatment (code 4-5, Table 1) and 2-stage hydrotreatment (code 6-7, Table 1) hydrogenation occurs faster than polymerization. This is clearly shown by a significant deoxygenation level and molecular weight break down, resulting in products with a lower tendency for coking than the products of the stabilisation experiments. A clear relation between molecular weight and TGA residue of the products was observed. This implies that higher molecular weight fragments are precursors for coke formation. Actual FCC experiments with low-residual product (code 8, Table 1) as co-feed are in progress to verify whether the product is indeed suitable as a feedstock for refinery units.

References:

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