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Product Distribution and Deactivation of Y-zeolite Based Catalyst in the Catalytic Cracking of Biomass Pyrolysis Oil

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The valorization of bio-oil by catalytic cracking is a promising route for producing hydrocarbon fuels as an alternative to oil. This work addresses the cracking of bio-oil over HY zeolite catalyst (Si/Al = 15) in a continuous reaction system composed of two-step on line (thermal + catalytic). The effect that temperature has on the bio-oil conversion and the distribution of reaction products is studied. The catalyst was synthetized by agglomerating the zeolite powder with inert filler and binder, and the raw bio-oil was stabilized by adding 20 wt% MeOH. Operating condition were: 500 ºC (thermal unit); 400-500 ºC and space-time, 0.7 $g_{catalyst}h/g_{feed}$ (fluidized bed reactor). Attention is also paid to the catalyst deactivation, analyzing the spent catalyst samples by different techniques (N_2 adsorption-desorption, adsorption/cracking/desorption of *t*-BA, and TGA-TPO). The results evidence a significant influence of temperature on the yield and composition of products. Although the LPG (C_3-C_4) hydrocarbons are the main products at 400 ºC, the increase in temperature notably promotes the conversion of oxygenates into C_{5+} hydrocarbons, which are the majority products above 450 ºC. Operation at 500 ºC has the advantages of both maximizing the production of a liquid fuel composed of 74 % C_5-C_{12} gasoline fraction (rich in 1-ring aromatics and C_6-C_7 cycloalkanes), and also attenuating the catalyst deactivation. Furthermore, the catalyst deactivation at 400 ºC and 450 ºC is faster than that observed at 500 ºC, despite the lower formation of coke. This fact is explained by the different nature and location of the coke deposited in the porous structure of the catalyst.

1. Introduction

The valorization routes for converting biomass into hydrocarbon fuels and/or raw chemicals (C_2-C_4 olefins and BTX) has undergone great technological development in recent decades (Valle et al, 2019). The catalytic cracking of biomass pyrolysis oil (bio-oil) is a promising and versatile route whose interest lies in the renewable nature of the bio-oil, which can be produced in geographically delocalized low-cost pyrolysis units. Subsequently, it can be transported for its centralized valorization in catalytic cracking units. A key factor for the successful development of these cracking processes is the availability of stable and selective catalysts, which would create economically attractive opportunities for large-scale production of high-quality fuels.

The catalytic cracking of bio-oil is a highly shape-selective reaction with strong dependency on the catalyst properties and reaction conditions. Zeolite-based catalysts (HZSM-5, β-zeolite, Y-type zeolite, ferrierite, H-mordenite, etc.) have shown to be effective in the conversion of bio-oil to hydrocarbons. Pore size and structural properties of acid zeolites are important features in regulating diffusion of reactants and products The conversion of bio-oil oxygenates is largely dependent on whether these compounds can enter, react and diffuse from the acid sites, thus affecting the distribution and yields of final products.

The HY zeolite is characterized by large and spherical internal cavities (≈ 1.3 nm) linked through 12-membered-ring pores (≈ 0.7 nm), which gives it its unique shape selectivity. Y-zeolite has been the primary active component of cracking catalysts used in a petroleum refinery (FCC units) to convert heavy fractions of crude oil into gasoline, diesel and liquefied petroleum gas. In addition, some studies have shown that Y-zeolite based catalysts are effective in deoxygenating bulky molecules, particularly phenolic ethers that are not converted on other zeolites like ZSM-5 due to steric hindrance (Yu et al., 2012). Although Y zeolites produce more C_6–C_9

aliphatic hydrocarbons (gasoline fraction) and less aromatics than ZSM-5, they are prone to deactivation by coke deposition within the supercages between the micropore intersections (Widayatno et al., 2015).

Furthermore, the complex composition of raw bio-oil (high contents of water and oxygenated compounds) and its properties (acidity and corrosivity) make it unsuitable for direct valorization. Consequently, several methods have been proposed for stabilizing and/or conditioning the raw bio-oil. Among these, the addition of light alcohols (i.e. methanol, ethanol) is an effective method for enhancing stability during storage, facilitating the bio-oil valorization into fuels and raw chemicals (Oasmaa et al., 2016), and attenuating the catalyst deactivation (Gayubo et al., 2009).

In this work, a two-step (thermal-catalytic cracking) system is used for producing fuels from raw bio-oil stabilized by methanol addition. This continuous reaction system enables studies on the evolution with time-on-stream of catalyst behaviour. In this case, Y zeolite with Si/Al = 15 has been agglomerated in a mesoporous matrix to improve the stability of the catalyst. Specifically, the effect that reaction temperature has on the evolution of oxygenates conversion and product yields is analysed.

Besides, it is important to gain knowledge about the origin and nature of the coke deposited on the catalyst, which causes the rapid deactivation inherent to the valorization of raw bio-oil. Therefore, spent catalyst samples have been characterized by different techniques with aim of relating the results with the catalytic behavior.

2. Experimental

2.1 Bio-oil feed and reaction equipment

The raw bio-oil (obtained by fast pyrolysis of pine sawdust and provided by *Biomass Technology Group-BTG*, Holland) was stabilized by adding 20 wt% MeOH (*Sigma-Aldrich*, ≥ 99.8%). The water content of stabilized bio-oil (18 wt%) was quantified by Karl Fischer titration (*KF Titrino Plus 870*), and their oxygenated composition was determined by GC-MS (*Shimadzu GC/MS QP2010*).

The two-step reaction equipment (Figure 1) consists of: (1) Thermal treatment unit, which is a U-shaped steel tube where the stabilized bio-oil feed (droplets boosted by a N_2 inert flow) is volatilized (residence time = 1 min) and the pyrolytic lignin (PL) is deposited; (2) Catalytic cracking unit (fluidized bed reactor), where the the volatile stream leaving the thermal step is transformed into hydrocarbons. The thermal unit was kept at 500 ºC, which is a suitable temperature for maximizing the bio-oil fraction liable to catalytic valorization, leading to a good compromise between product yields and catalyst stability (Valle et al., 2017).

The catalyst (150-300 μm) was mixed with an inert solid (CSi carborundum, 100 μm) to ensure good fluidodynamic conditions in the catalytic bed. The cracking experiments were carried out with the same space-time value of 0.7 $g_{catalyst}h/g_{feed}$ (0.9 $g_{catalyst}h/g_{bio\text{-}oil}$) and varying reaction temperature (400, 450 and 500 ºC). The reaction product stream was analyzed on-line using a gas micro-GC (*Agilent mGC 490*) provided with four analytical modules for the analysis of: (1) H_2, N_2, CH_4, CO (MS5A); (2) bio-oil oxygenates and C_{5+} hydrocarbons (CPSil); (3) CO_2, C_2-C_4 hydrocarbons, H_2O, MeOH, DME (PPQ); (4) BTX aromatics (Stabilwax).

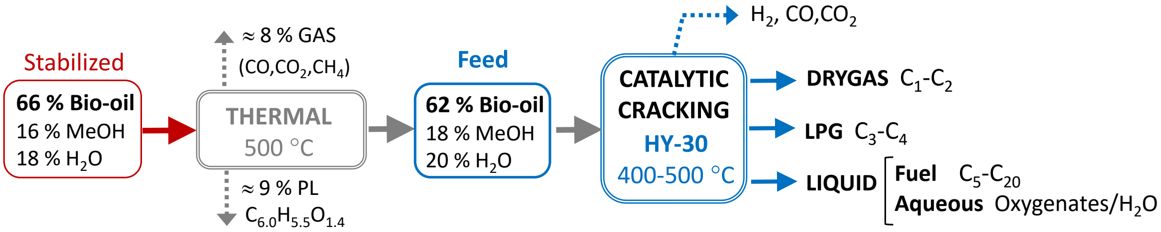

Figure 1: Continuous two-step process for the catalytic cracking of bio-oil.

2.2 Catalyst synthesis and characterization

The Y-zeolite based catalyst was prepared by mixing 50 wt% of HY zeolite with Si/Al =15, 20 wt% of inert filler (α-Al_2O_3) and 30 wt% of binder (pseudoboehmite). The wet mixture was extruded and dried at room temperature for 12 h. After drying, the extrudates were ground, sieved (150-300μm) and calcined at 575 °C for 2 h. During the calcination, pseudoboehmite was converted into γ-Al_2O_3, which is the stable phase at that temperature. Following this agglomeration method, the zeolite crystals are dispersed into an inert matrix with mesoporous structure and improved mechanical resistance, which enhances catalyst stability by promoting diffusion of coke precursors outside the zeolite micropores (Cordero-Lanzac et al., 2018).

The textural properties of fresh and spent catalyst samples were measured by N_2 adsorption-desorption (*Micromeritics ASAP 2010*) after outgassing each sample at 150 ºC for 8 h under vacuum. The Brunauer-Emmet-Teller (BET) equation was used to calculate the specific surface area (S_{BET}) from the adsorption data (P/P_0=0.05–0.25). The total pore volume was based on the volume adsorbed at P/P_0= 0.995, and the micropore volume (V_{micro}) was calculated using the *t*-plot method, based on the Harkins-Jura equation. The mesopore volume (V_{meso}) was calculated as the difference between the total pore volume and the micropore volume. The resulting properties of the fresh catalyst were: S_{BET} = 488 m^2/g, V_{micro} = 0.15 cm^3/g and V_{meso} = 0.34 cm^3/g.

The acidity of fresh and spent catalyst samples was determined by adsorption-cracking-desorption of *tert*-butylamine (tBA) (Setaram DSC-111 calorimeter) coupled to a mass spectrometer (Balzers Thermostar) for recording the signal of *t*BA cracking product (butene, m/z = 56) during the temperature-programmed-desorption (TPD) run. This technique allows evaluating the capability of the acid sites for cracking hydrocarbons chains. All the *t*BA-TPD profiles (not reported) corresponding to fresh and spent catalyst samples showed a single well-defined peak at ≈ 245 ºC attributed to strong acid sites.

The amount of coke deposited over the spent catalyst samples was determined by thermogravimetric analysis of temperature programmed oxidation (TGA/TPO) using a *TA Instruments Q5000 IR* thermobalance.

3. Results and discussion

3.1 Composition of bio-oil feed

Table 1 shows the semi-quantitative composition (% peak area of GC-MS analyses) of the raw bio-oil, and the composition of oxygenates contained in the stabilized bio-oil, which are 66 % of the total (Figure 1), the rest being water and methanol (not shown in the results).

The results are consistent with those obtained by other authors (Moens et al., 2009) and show that apart from a dilution effect, the addition of MeOH causes changes in the raw bio-oil composition. Thus, the amount of acids, ketones and aldehydes is lower in the stabilized bio-oil, whereas esters and ethers increase because reactive carboxylic acids and carbonyl compounds become their corresponding esters and acetals (esterification). As a result, the stabilized bio-oil contains 16 % MeOH and 66 % bio-oil (Figure 1).

The thermal step induce polymerization of ≈ 9 wt% of the bio-oil fed (mainly phenolic compounds) leading to pyrolytic lignin (PL) deposition (Figure 1), and also decomposition of ≈ 8 wt% of bio-oil into gases (CO, CO_2, and CH_4). As a result, the stream leaving this step (which is the feed to the cracking reactor) is composed of 62 % of oxygenates derived from bio-oil, whose composition is shown in Table 1.

Table 1: Composition of raw bio-oil (1), oxygenates contained in stabilized bio-oil (2), and oxygenates stream leaving the thermal step (3).

	(1) Raw bio-oil	(2) Stabilized bio-oil	(3) Oxygenates stream
Acids	19.4	16.5	23.1
Acetic acid	*16.6*	*14.6*	*22.2*
Ketones	21.4	12.2	18.2
Esters	11.3	13.3	25.4
Methyl formate	-	*8.5*	*10.0*
Furanones	4.4	2.3	1.2
Alcohols	3.2	4.0	5.9
Aldehydes	6.8	2.6	1.9
Ethers	1.4	4.4	5.1
Saccharides	13.7	30.7	12.0
Levoglucosan	*11.1*	*26.8*	*9.6*
Phenols	18.4	14.0	7.3
Guaiacols	*11.1*	*6.7*	*3.4*

3.2 Bio-oil conversion and distribution of reaction products

The reaction products were grouped into dry gas (C_1-C_2), liquefied petroleum gases LPG (C_3-C_4), C_{5+} hydrocarbons, CO+CO_2, H_2, and water. The conversion of oxygenates derived from bio-oil was quantified from the mass flow-rate at the inlet (F_i, g/min) and outlet (F_{out}, g/min) of the catalytic reactor, Eq(1). Similarly, the conversion of MeOH was individually quantified from its corresponding mass flow-rates, Eq(1). The yield of each product lump was quantified by Eq(2).

$$X_i = \frac{F_{i,in} - F_{i,out}}{F_{i,in}} x\ 100 \qquad (1)$$

$$Y_j = \frac{F_{j,out}}{F_{bio\text{-}oil,in} + F_{MeOH,\,in}} x\ 100 \qquad (2)$$

The evolution with time-on-stream of the conversion of bio-oil derived oxygenates, and the conversion of MeOH are shown in Figure 2a and 2b, respectively. The yields of reaction products are shown in Figures 2c-e.

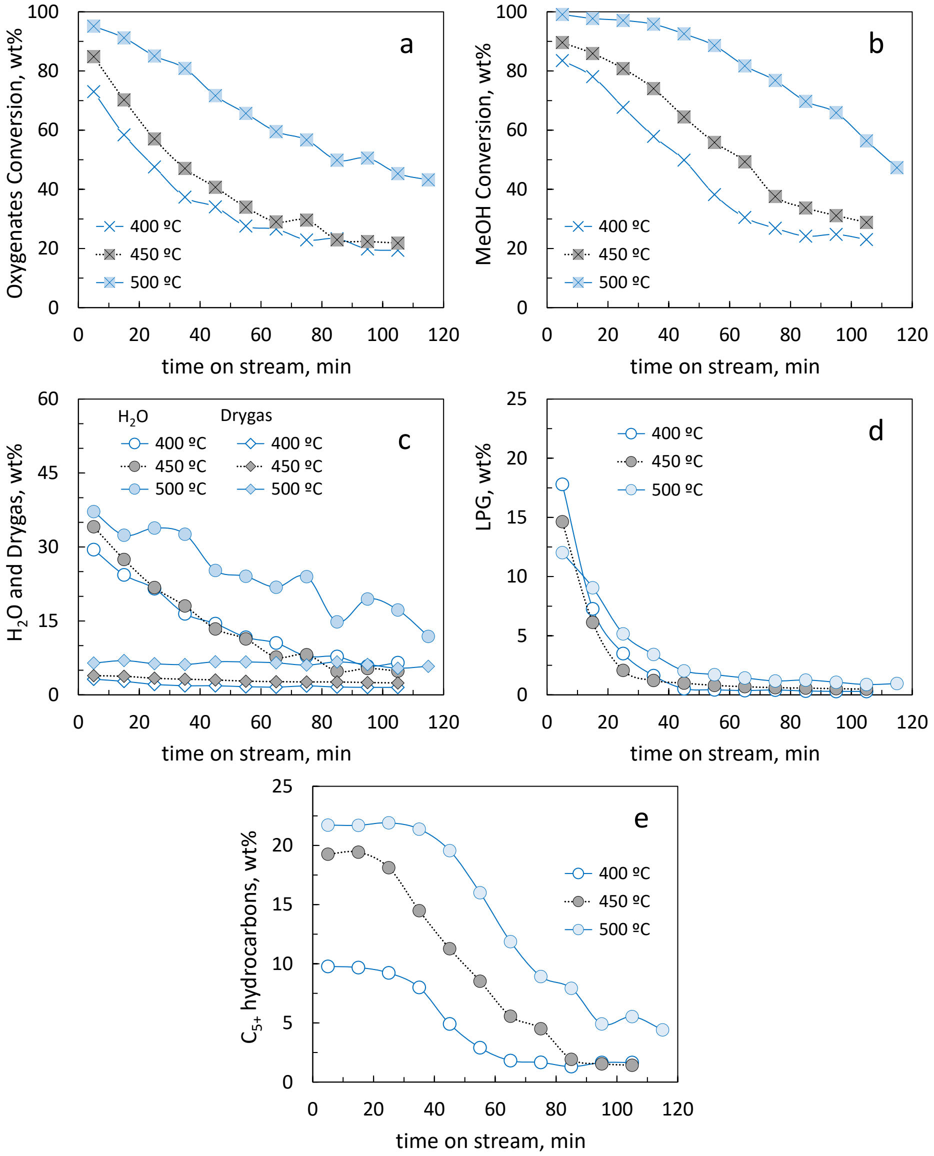

Figure 2: Evolution with time-on-stream of oxygenates conversion (Graph a), MeOH conversion (Graph b), and product yields (Graphs c-e).

The results show a high initial conversion of oxygenates and MeOH at 400 ºC (73 wt% and 84 wt%, respectively), with the LPG hydrocarbons being the main C-containing products (18 wt% yield compared to 10 wt% of C_{5+} hydrocarbons. As the reaction temperature is raised, the initial values of both the oxygenates and MeOH conversion progressively increase. The raise in the 400-450 ºC range promotes the conversion of MeOH and bio-oil oxygenates into C_{5+} hydrocarbons (Figure 2e), which are majority products above 450 ºC. A further increase up to 500 ºC promotes the formation of C_{5+}, but especially the dehydration reactions of MeOH and oxygenates, which lead to a notable formation of water in the reaction medium (Figure 2c).

Figure 3 shows the composition of C_{5+} hydrocarbons contained in the liquid fuel collected through reaction at 500 ºC, specifically after 1 h on stream and at the end of the reaction. The liquid collected at 1 h (Figure 3a) is mainly composed of C_5-C_{12} gasoline (74 %), with majority of 1-ring aromatics and aliphatic compounds (mainly C_6-C_7 cycloalkanes). The content of heavier C_{13}-C_{20} diesel fraction is 26 %, which is composed of 2-ring aromatics (naphtalenes) and C_{13}-C_{16} linear paraffins. As shown in Figure 2d, the yield of the liquid fuel decreases as the catalyst deactivates, and its composition undergoes some changes. The liquid collected at the end of reaction (2 h, Figure 3b) has a higher content of diesel fraction (37 %) due to the higher formation of poliaromatics (PAHs) (with 96 % of 2-ring compounds). In addition, a lower content of aliphatic hydrocarbons is observed both in the gasoline fraction and in the diesel one.

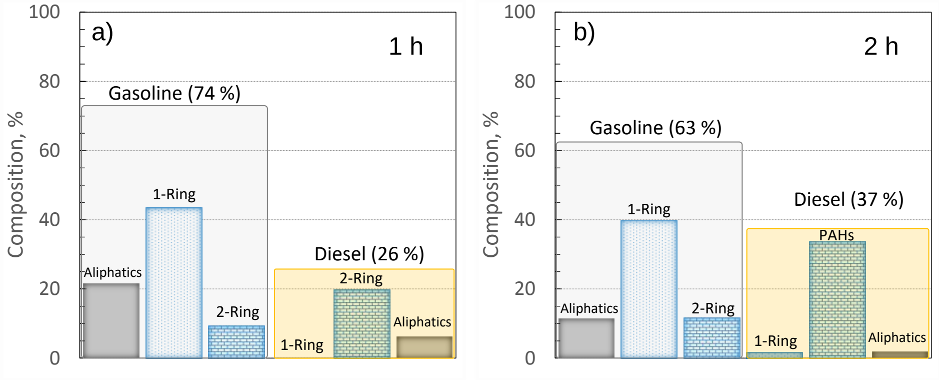

Figure 3: Composition of the liquid fuel collected after 1 h (Graph a) and 2 h (Graph b) of reaction at 500 ºC.

3.3 Analysis of catalyst deactivation

Based on the evolution with time-on-stream of oxygenates conversion and product yields (Figure 2), the catalyst deactivates rapidly for LPG formation, whereas its activity for producing C_{5+} hydrocarbons is maintained for a longer time, regardless of reaction temperature. Furthermore, the deactivation rate at 400 and 450 ºC is similar and faster than that observed at 500 ºC. Although this result seems contrary to the increasing tendency of total coke content (Table 2), it can be explained by the TGA-TPO analyses. The TPO profiles reveal the heterogeneous nature of the coke, composed of two main fractions: Coke-1, with combustion temperature below 500 ºC, which in turn is composed of two subtypes: Coke-1a (burning at 400-415 ºC) and Coke-1b (burning at 445-475 ºC), and Coke-2 (above 520 ºC). The different combustion temperature is ascribed to its different composition and/or location within the catalyst particle (Valle et al., 2010). The amount of each coke fraction deposited, as well as the residual acidity and textural properties (BET and external surface area, and pore volume) of spent catalyst samples are shown in Table 2. The values corresponding to the fresh catalyst are also shown for comparison.

Table 2: Properties of fresh and spent catalyst.

	Fresh	400 ºC	450 ºC	500 ºC
Acidity (mmol$_{tBA}$/g)	0.47	0.07	0.08	0.11
S_{BET} (m^2/g)	488	93	103	110
V_{micro} (cm^3/g)	0.15	0.012	0.014	0.019
V_{meso} (cm^3/g)	0.34	0.161	0.169	0.171
Coke content (wt%)	--	21.1	24.4	29.0
Coke-1a		*5.2*	*4.8*	*4.1*
Coke-1b		*6.5*	*9.2*	*13.1*
Coke-2		*9.8*	*10.5*	*11.9*

The trends observed in coke deposition are in agreement with the deactivation rates (Figure 2). The amount of Coke-1a fraction decreases as the reaction temperature is raised, whereas deposition of both Coke-1b and Coke 2 increase, especially the Coke-1b fraction. The Coke-1a fraction can be related to the presence of oxygenates in the reaction medium, on account of the lower the conversion of bio-oil (Figure 2) the greater the amount of this type of coke (Table 2). This “oxygenated” coke is formed from thermally unstable oxygenates (mainly phenolic compounds) that are prone to re-polymerization on the external surface of the catalyst (Valle et al, 2012). Conversely, the greater the conversion of oxygenates the higher deposition of Coke-1b and Coke-2, thus pointing to their catalytic origin. Therefore, the formation of these fractions is related to the degradation of reactants (bio-oil oxygenates) and evolution of reaction products (C_{5+} hydrocarbons and LPG) through dehydrogenation, cyclization, aromatization and condensation reactions activated by the acid sites (Ibañez et al, 2012). Coke-1b (with lower combustion temperature) could be deposited on the external surface of the zeolite crystals, whereas Coke-2 is an internal coke deposited inside the microporous of the zeolite.

As a result, the HY catalyst deactivation at 500 ºC is lower than at 400 ºC and 450 ºC (Figure 2), which is consistent with the textural properties and higher residual acidity of the spent catalyst at this temperature (Table 2), and explained by the lower thermal/catalytic coke ratio. Furthermore, the catalytic coke formation at 500 ºC is presumably attenuated by the partial cracking of coke precursors, and by the high water content in the reaction, which may cause partial gasification of coke deposits and/or may compete with coke precursors on their adsorption on the acid sites.

4. Conclusions

Y-zeolite based catalyst with Si/Al = 15 has been synthesized and explored for the continuous upgrading of bio-oil in a two-step (thermal + catalytic) continuous reaction system. The acidity and porous structure of HY catalyst (with the active phase of HY zeolite agglomerated in an inert mesoporous matrix) give it good behaviour for producing fuels by catalytic cracking of stabilized bio-oil feed.

The results evidence a significant influence of temperature on the product distribution and composition of fuels. Although the LPG (C_3-C_4) hydrocarbons are the main products at 400 ºC, the increase in temperature notably promotes the conversion of MeOH and bio-oil oxygenates into C_{5+} hydrocarbons, which are the majority products above 450 ºC. Catalytic cracking at 500 ºC is suitable for maximizing the production of a liquid fuel mainly composed of C_5-C_{12} gasoline (rich in 1-ring aromatics and mainly C_6-C_7 cycloalkanes). Besides, this temperature is suitable for attenuating the catalyst deactivation, probably due to the notable formation of water by oxygenates dehydration reactions.

Furthermore, the HY catalyst deactivation rate at 400 ºC and 450 ºC is similar and faster than that observed at 500ºC, despite the lower formation of coke. The TPO results reveal the heterogeneous nature of the coke deposited on the HY catalyst, which is composed of a coke fraction deposited on the mesoporous matrix (Coke-1), and a fraction formed within the microporous structure of the zeolite (Coke-2).

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