STUDY OF CATALYTIC HYDROTREATMENT OF PYROLYSIS BIO-OIL

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Abstract

Pyrolysis bio-oil is a promising 2nd generation biofuel. To achieve a more widespread use of bio-oils, their negative properties caused by high oxygen content must be improved. Over the last 30 years of study of bio-oil upgrading, catalytic hydrotreatment seems to be preferred to catalytic cracking, as hydrotreatment affords higher yields of desired products having better quality and higher degree of deoxygenation. The main problem observed during hydrotreatment of bio-oils is the formation of condensed high-molecular-weight products, which causes plugging of the catalyst bed and thus, shutting down of the reactor. This work summarises possible problems observed during hydrotreatment of bio-oils, their causes and possibilities how to minimize them. The work also presents results obtained from initial continuous hydrotreatment experiments of a bio-oil from ablative flash pyrolysis of straw.

Introduction

Global energy consumption continues to rise and about 78 % of consumed energy comes from fossil sources[1]. Reserves of fossil fuels are limited and their combustion has adverse effects on environment, as they contribute to an undesirable increase in CO_2 concentration in the atmosphere. To reduce CO_2 emissions, fossil fuels need to be replaced, at least partially, by renewable sources. Biomass is the only renewable feedstock containing carbon, and thus the only alternative to crude oil derivatives[2]. Fast pyrolysis is a promising BTL (biomass to liquid) technology producing bio-oil via thermal decomposition (pyrolysis) of biomass in the absence of oxygen[3]. Pyrolysis bio-oil could be used after appropriate upgrading as a 2nd generation biofuel.

Pyrolysis bio-oil

In fast pyrolysis process, yields of bio-oil can be up to 75 wt% on dry-feed basis. Bio-oil is a black or dark brown oily liquid. It is a complex mixture of oxygen-containing compounds and often large amounts of water[3]. Chemical composition causes many problematic properties, such as thermal and chemical instability, high viscosity, low H/C ratio and very low miscibility with hydrocarbons. Bio-oil also has high acidity (pH=2–3) which causes corrosion of metallic storage tanks and pipelines. High content of phenolic compounds causes destruction of seals and gaskets [4]. Thus, direct combustion of bio-oils in vehicle engines is not possible. However, bio-oils have a volumetric energy density 5 to 20 times higher than the original biomass, so its seems to be a good intermediate product that can be transported to a large central processing unit[2].

Options of bio-oil upgrading

The main challenge of biofuels production from bio-oils is the (i) reduction of oxygen content and molecular weight and (ii) maximum transition of carbon into a liquid product with the highest possible yield. Reduction of the oxygen content leads to a decrease in acidity and to an increase in the calorific value of oil[5]. Conversion of carbonyl compounds leads to an increase in the product stability[2].
To improve the properties of bio-oils, the following processes can be applied:
  i.   catalytic hydrotreatment,
  ii.   catalytic cracking,
  iii. esterification,
  iv.   gasification followed by Fischer-Tropsch synthesis to produce hydrocarbons and alcohols.
The results of Mortensen et al.[5] indicate that catalytic hydrotreatment seems to be preferred to catalytic cracking, as catalytic hydrotreatment gives higher yields and better quality of product with higher degree of deoxygenation. In addition, less gas and solid side products are created. The disadvantage is that hydrotreatment is cost-demanding because it requires considerable amounts of hydrogen[5].

Catalytic hydrotreatment of bio-oil

The main goal of catalytic hydrotreatment of bio-oil is to reduce the oxygen content and thus reduce the atomic O/C ratio and increase the H/C atomic ratio of bio-oil. The main reaction in catalytic hydrotreatment of bio-oil is hydrodeoxygenation (HDO). To decrease the hydrogen consumption, it is desirable to avoid hydrogenation of aromatic rings[6]. Oxygen is removed mainly as water and when high degree of HDO is achieved, spontaneous phase separation occurs. The created water also dissolves alkali metals present in bio-oil.[7] Besides the main HDO reaction, cracking, hydrodecarbonylation, hydrodecarboxylation, hydrocracking, hydrogenation and undesirable polymerization and coke formation can occur as well[5].

Full deoxygenation is theoretically feasible, but at the cost of a significant reduction in the yield of the organic liquid phase. The key aim is thus to maximize the energy yield of the organic liquid phase. A high degree of deoxygenation is supported by a long residence time[2]. Hydrodeoxygenation of bio-oil is performed at a high pressure typically[2] from 7 to 23 MPa. High pressure is necessary to keep the water in liquid phase, to promote hydrogenation reactions and also to suppress charring reactions[2]. Although for complete HDO of bio-oil about 25 moles H_2 per kg of bio-oil is required, typically used amount of hydrogen ranges from 35 to 420 moles per kg of bio-oil[2]. Bio-oil hydrotreating is typically carried out at temperatures between[2] 250 and 450 °C.

The reaction takes place on catalysts and sulphided CoMo and NiMo catalysts supported on Al_2O_3 are commonly used[6]. An alternative might be catalysts based on noble metals (Ru, Rh, Pd and Pt). Although these catalysts showed, in comparison to sulphide catalysts, higher yields of oil and a higher degree of deoxygenation at lower temperatures, their higher price prevents their commercial use[8] CuCr, CuO, NiO, Ni and NiCu may be an alternative to precious metals due to their lower price[9]. Yakovlev et al.[10] tested catalysts based on Ni and found that all used types were less active than Pd/Al_2O_3, but they had a greater stability than the CoMo/Al_2O_3. It was found that the addition of phosphorus to the catalysts based on Ni, Mo, Co allowed preparing catalysts with higher metal concentrations. In addition it led to improved dispersion of metals on a support, enhanced catalyst resistance to coke deposition and increased the strength and stability of the catalyst[11].

Problems of bio-oil hydrotreatment, their causes and possible solutions

Besides the low yield of hydrogenated oil, the biggest problem of hydrotreatment of bio-oil is the rapid deactivation of the catalyst and reactor fouling due to formation of large amounts of condensed high-molecular-weight products. Coking can be so extensive that it causes catalyst bed plugging and thus forcing a shutdown of the reactor[12]. HDO catalyst deactivation is a major problem, and its mechanism is still unclear. It has been associated with the modification of the active phase or the support by water, poisoning of active phase by nitrogen compounds, sintering of the active phase, deposition of alkali metals and coking[9].

Deposition of coke particles is the main cause of catalyst deactivation. Previous research in hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) showed that coking has been associated with the formation of polyaromatic compounds that are deposited on the catalyst and block the active sites[13].

The formation of carbon deposits depends upon the type of hydrotreated materials and also on the type of catalyst. On an active support, unsaturated compounds (olefins and aromatics) are strongly adsorbed, and this leads to higher coke formation[5]. It was found that all phenolic compounds bind to alumina and block the active sites of the catalyst. Popov et al.[14] found that two thirds of alumina surface was covered by phenolic compounds in the hydrogenation of phenol at 400 °C. This layer had a high tendency for coking. Phenolic compounds were adsorbed on the surface of alumina due to its relatively high acidity[14]. Only the most basic compound (2-ethylphenol, 4-ethylphenol and guaiacol) also interact with the sulphide phase of catalyst[15]. Consequently, use of less acidic supports was suggested. For example, only 12 % of the SiO_2 surface was covered by adsorbed phenolic compounds at the same conditions as used for Al_2O_3. SiO_2 binds phenols only via hydrogen bonds[16], i.e. the adsorption strength of phenols on SiO_2 is weaker than on Al_2O_3. Another alternative are active-carbon-supported catalysts. The neutral character of carbon support results in a lower tendency to coke formation in comparison with alumina[17]. However, the disadvantage of carbon is that it cannot be easily regenerated[8]. ZrO_2, TiO_2 and CeO_2 were described in the literature as other potential supports[19,20]. These compounds have a great potential for activation of oxygen groups on the catalyst surface, because they contain less acidic sites than γ-Al_2O_3[10]. ZrO_2 contains besides acidic sites also basic sites, which can prevent the deposition of coke[8].

Other compounds present in bio-oil causing the polymerization reactions and coke formation are oxygenates with more than one oxygen atom in molecule. Hydrotreatment conditions play also an important role. Generally, the temperature increase leads to an increase in coke formation[13].

To deal with the high propensity of bio-oil to coking, a two-step process has been accepted for the hydrotreating of bio-oils over the last 30 years. In the initial step, a stabilization of bio-oil occurs at 150 to 250 °C, which is necessary to minimize the reactivity of bio-oil, i.e. to suppress polymerization and condensation reactions. This step leads to the elimination of the most reactive functional groups causing instability of bio-oil, such as aldehydes,

ketones, and unsaturated compounds[18]. In the second step, higher temperatures of about 350 to 450 °C can be applied[7, 19] and the degree of deoxygenation is up to 95 %. Additionally, high-molecular substances derived from lignin are converted to simpler substances which leads to a reduction of the Conradson carbon residue of the product[2].

Another problem is caused by the presence of water. It has been shown that water has an inhibitory effect on conventional sulphide catalysts[13] A possible explanation is the leaching of the sulphur from the catalyst by the action of (liquid) water[13]. This effect can be mitigated by the addition of H_2S to the feed[13]. Water also negatively affects alumina, which is transferred to boehmite (AlO(OH))[2]. Laurent and Delmon[20] showed that the formation of boehmite causes oxidation of the nickel on the catalyst. The nickel oxides are inactive for HDO reaction and may further block the active sites of molybdenum and nickel sulphides[20].

During HDO of bio-oil on sulphided catalysts, the deactivation of a catalyst by nitrogen compounds adsorbed on the active sites was observed. This problem is well known from the HDS of petroleum fractions[13].

Because of all these problems, experiments in batch reactors still dominate. During the crude bio-oil upgrading in a continuous-flow fixed-bed reactor, only a 100 h long continuous operation was achieved[21]. After catalytic hydrogenation pre-treatment followed by a two-stage catalytic hydrotreatment, Olarte et al.[22] reached up to 1440 h (60 day) of operation without plugging the transition zone between the two stages. However, after 750 h, a significant deactivation of 1st zone was observed and required replacement of the catalyst in it[22].

Experimental

Activation of catalyst and determination of its activity

The catalyst was activated in-situ by hydrotreated gas oil with 3.7 wt% of DMDS. After activation, the catalyst was stabilized by hydrotreating of crude atmospheric gas oil (AGO, sulphur content 0.23 wt%) to determine the hydrotreating activity of the catalyst prior to bio-oil hydrotreating. After completing the set of experiment hydrotreating of bio-oil, AGO was hydrotreated to determine the decrease in the catalyst hydrotreating activity due to the deactivation caused by bio-oil hydrotreating.

Hydrotreatment of bio-oil

Catalytic hydrotreatment of bio-oil from ablative pyrolysis of straw (barley/wheat 1/1 wt%) with 0.5 wt% of DMDS was performed in a continuous-flow fixed bed reactor (i.d. 23 mm and length 320 mm). Conditions were as follows: temperature at 200 – 360°C, constant pressure at 4 MPa, hydrogen flow rate 90 l·h^{-1} and WHSV equal approximately to 1 h^{-1} using a 55 g of commercial NiMo catalyst (Ni 6.9 wt% and Mo 27.7 wt%). Particle size of catalyst was as follows top and down layer 5.0 g not-crushed catalyst (p.s. 1 mm), transitional layer 5.5 g (p.s. 0.84 - 1.50 mm) and middle (main) layer 34 g (p.s. 0.25 - 0.42 mm). Products were labelled as follows TTT/4 = temperature (°C)/pressure (MPa).

Analysis of feed and products

Elemental composition (C, H, N) was determined using an Vario EL Cube (Elementar). The oxygen content was calculated as a difference to 100 wt%. The water content was determined by Karl Fischer volumetric titration. HYDRANAL Coulomat AK (Riedel den Haën) was used as a titrant. Density and viscosity were measured using SVM 3000 Stabinger Viscometer (Anton Paar). Carboxylic acid number was determined by automatic titration using Metrohm DMS Titrino 716, by method based on ASTM D664 modified for bio-oil, where tetrabutylammonium hydroxide is used as a titrant. The obtained results were recalculated to mg KOH·g^{-1} bio-oil sample.

Results and discussion

Bio-oil hydrotreatment

The experiments were performed in the order of increasing temperature. The real average temperatures on the catalytic bed at selected experimental conditions and time on stream of this experiments are shown in Table I. Fluctuations in flow were recorded during the bio-oil hydrotreatment, therefore the real average WHSV during each experimental condition was calculated, see Table I.

At temperatures below 300 °C, the product was highly viscous (kinematic viscosity at 40 °C more than 130 mm^2·s^{-1}) and it was inhomogeneous. At 300 °C the separation to aquatic and organic phase was observed. At 317 °C, the organic phase had firstly lower density then water and it was thus upper phase. With increasing of reaction temperature, the amount of organic phase of product decrease up to 50.6 wt% at 360 °C. It was caused by higher degree of deoxygenation and thus higher amount of aqueous phase was created. The best properties had in all

cases product gained at reaction temperature of 360 °C and 4 MPa pressure, for visual comparison with raw material see Figure 1.

Table I
Physical and chemical properties of feed and chosen organic phase of products

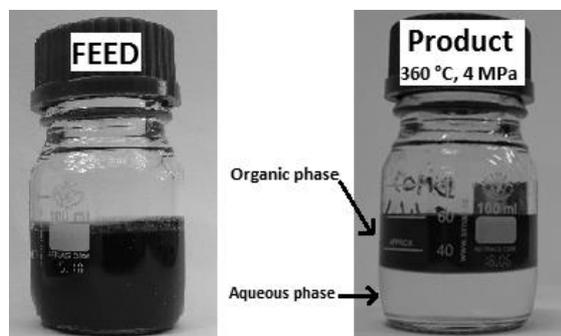| Experiment	240/4	280/4	320/4	360/4
T in catalyst bed (°C)	242	279	317	359
TOS (h)	18	28	41	80
WHSV (h^{-1})	1.07	0.80	0.98	1.14

Figure 1: Feed and product of hydrotreatment at 360 °C and 4 MPa

Physical and chemical properties of feed and selected products are compared in the Table II. With increasing temperature of hydrotreatment, density of organic phase decreased from 1.13 up to 0.95 $g \cdot cm^{-3}$. Kinematic viscosity at 40 °C decrease from 140 to 11 $mm^2 \cdot s^{-1}$. Water content (inseparably by centrifugation) decreased from 22 to 1.2 wt%. Oxygen content decreased from 20 to 4.5 wt%, which meant degree of deoxygenation up to 77.5 %. Also significant decrease in the amount of carboxylic acids from 55 up to 3.0 $mg\ KOH \cdot g^{-1}$ was recorded.

Table II
Physical and chemical properties of feed and selected organic phase of products

Sample	Feed bio-oil	Product			
		240/4	280/4	320/4	360/4
Yields of organic phase (wt%)	-	85.9	80.5	55.7	50.6
C *(wt%)	71.94	72.61	75.35	80.01	83.88
H * (wt%)	7.11	8.38	9.09	10.12	10.81
N * (wt%)	0.83	0.80	0.90	0.94	0.80
O * (wt%)- to 100 %	20.11	18.19	14.66	8.93	4.51
Density at 15 °C ($g \cdot cm^{-3}$)	1.133	1.088	1.055	0.999	0.952
Kinematic viscosity at 40 °C ($mm^2 \cdot s^{-1}$)	140.47	153.5	130.8	37.3	10.82
Water (wt%)	22.0	6.4	4.5	2.5	1.2
Carboxylic acid number ($mg\ KOH \cdot g^{-1}$)	55.3	48.2	38.5	24.9	3.0
Carboxylic acid number as acetic acid (wt%)	5.9	5.2	4.1	2.7	0.3

*The elemental composition is given on dry basis, i.e. subtracting bio-oil water content determined by Karl-Fischer titration

Catalyst deactivation

The fresh catalyst exhibited high hydrotreating activity, the sulphur content decreased from the initial 0.23 wt.% to about 3 $mg \cdot kg^{-1}$ at the end of the catalyst stabilization period. After hydrotreating of bio-oil for 84 hours in the temperature range 200 – 360°C, hydrotreating of the AGO resulted in a decrease in its sulphur content to 80

mg·kg^{-1}. This clearly shows that the catalyst has suffered from severe deactivation as the content of sulphur the products of AGO hydrotreating increased.

Conclusion

Hydrotreatment of bio-oil from straw was performed in continuous-flow fixed bed reactor. Conditions were as follows: constant pressure 4 MPa, hydrogen flow rate 90 l·h^{-1}, WHSV equal approximately to 1 h^{-1} and the influence of temperature (200 – 360 °C) on the properties of the product was studied. Product properties with increasing temperature of hydrotreatment were improving. The best properties had product gained at reaction temperature of 360 °C and 4 MPa pressure, with yield of 50.6 wt%. Although the pressure drop on the reactor was not recorded, the catalyst activity for hydrodesulfuration of AGO decreased ca. 26 times.

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