RESEARCH ARTICLE

Hydro-pyrolysis of lignocellulosic biomass over alumina supported Platinum, Mo$_2$C and WC catalysts

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Abstract   In-line hydro-treatment of bio-oil vapor from fast pyrolysis of lignocellulosic biomass (hydro-pyrolysis of biomass) is studied as a method of upgrading the liquefied bio-oil for a possible precursor to green fuels. The nobel metal (Pt) and non-noble metal catalysts (Mo$_2$C and WC) were compared at 500 °C and atmospheric pressure which are same as the reaction conditions for fast pyrolysis of biomass. Results indicated that under the pyrolysis conditions, the major components, such as acids and carbonyls, of the fast pyrolysis bio-oil can be completely and partially hydrogenated to form hydrocarbons, an ideal fossil fuel blend, in the hydro-treated bio-oil. The carbide catalysts perform equally well as the Pt catalyst regarding to the aliphatic and aromatic hydrocarbon formation (ca. 60%), showing the feasibility of using the cheap non-noble catalysts for hydro-pyrolysis of biomass.

Keywords   bio-oil, pyrolysis, hydro-deoxygenation (HDO), non-noble metal catalysts, hydro-treatment

1   Introduction

Biofuels have gained considerable interest in recent years because of the high crude oil prices, energy security concerns and potential climate change consequences over the utilization of fossil fuels. In this context, conversion of waste biomass into liquid bio-crude (termed as bio-oil), an alternative to fossil oil, is a significant step. Fast pyrolysis of biomass, one of the liquefaction processes, has made significant progress in the last years. Fast pyrolysis bio-oil as we know it today is a complex mixture of water and a large variety of oxygen containing organic molecules with different chemical functional groups. Some reported adverse properties of pyrolysis oil which restrict its application are its high water content, high oxygen content, high acidity, low heating value and poor stability [1]. The poor characteristics of bio-oil are also a consequence of its high oxygen content.

Among the problems the most important factors are heating value and the stability of the bio-oil. Oxygenates such as aldehydes and ketones, containing carbonyl group cause preservability problems due to their tendency to undergo condensation reactions and viscosity increase of the oil [2]. Further the overall high oxygen content (O/C ratio) of the bio-oil results in a low high heating value.

As being illustrated in Fig. 1 [3], the quality of the bio-oil can be improved by reducing its oxygen content *via* deoxygenation (DO) in an inert atmosphere [4] or hydro-deoxygenation (HDO) under hydrogen [5]. During DO, oxygen is removed as carbon oxides and water. Loss of carbon along with oxygen, lowers bio-oil yields. 30 wt-% carbon recovery from the biomass in the bio-oil is typical. During HDO, oxygen is removed mainly as H$_2$O resulting in enhancement of liquid yields and ideally lower loss of carbon [6]. Noble metal catalysts are widely applied in upgrading the pyrolysis oil by HDO [7]. However, they are rare and costly, which give rise to the necessity of alternative materials as substitutes for noble metals.

Transition metal carbides have been shown to be promising since they present catalytic behaviour similar to noble metal catalysts [8]. In 1973 Levy and Boudart. found tungsten carbide shared properties with platinum [9]. The carbon in tungsten carbide changes the electron density of tungsten in a way that it is similar to the electron density of platinum. Tungsten carbide is able to catalyze reactions that are catalyzed by platinum, only with a lower activity. Tungsten carbide is already used as catalyst for hydro-de-sulfurization (HDS) and hydro-de-nitrogenation (HDN) reactions [10,11] of fossil components via hydrogenation [12,13]. Investigation on catalytic hydro-treating showed that tungsten carbide is also capable of deoxygenation of propanol and propanal [14], and (hydro)
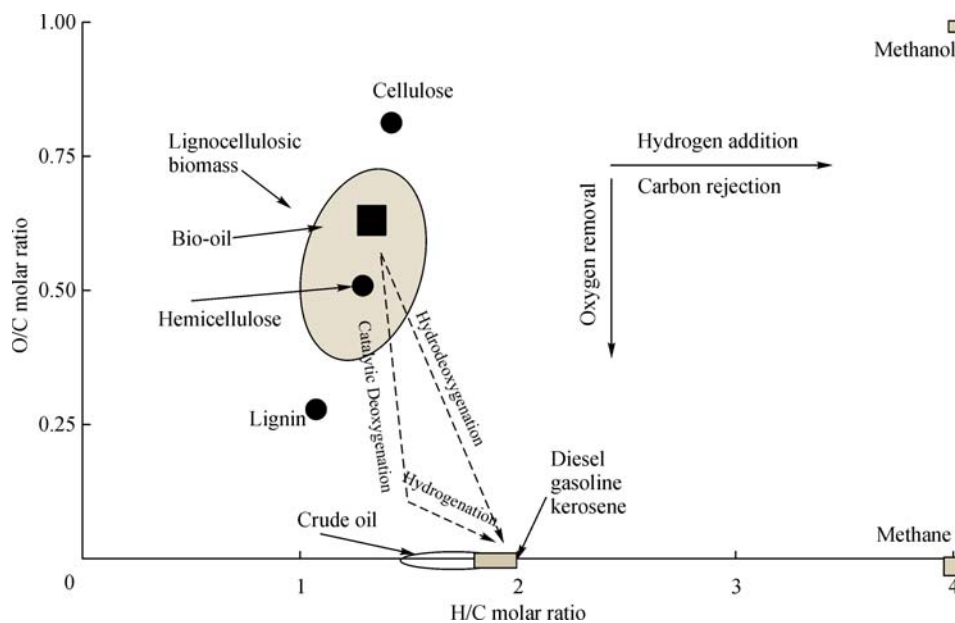
Fig. 1   Elemental composition of biomass, and pyrolysis oil in van Krevelen diagram [3]

deoxygenation of stearic acid [15] and oleic acid [16]. In a recent study the bonding between tungsten carbides and carbon, oxygen and hydrogen were investigated computationally [17]. It was shown that tungsten carbide, unlike platinum, tended to bind carbon and oxygen more weakly and hydrogen more strongly. This implies that hydrogen binds to the surface and that carbon and oxygen depart together as CO or CO_2. That is probably the reason why tungsten carbide works as catalyst in deoxygenation reactions.

Molybdenum carbide has been used as a successful catalyst for de-oxygenation [18–20], hydrogenation [21,22] and hydro-de-oxygenation [16,23,24] reactions. These studies have focussed on model reactions with compounds which are typically present in bio-oil. Molybdenum carbide has also been shown to be able to upgrade the bio-oil produced from biomass [25].

In order to use carbide catalysts effectively, different types of support materials have been investigated [24–27]. In general, there are three types of support materials: moderate-high acidic, weakly acidic and neutral/basic. Moderate-high acidic materials such as zeolites (H-FAU, H-MFI) [28] have greater activity but extensive deoxygenation, e.g., dehydration, which lead to formation of olefins and aromatics and which in turn cause extensive coke formation. Catalyst acidity is essential for deoxygenation and thus weaker acids are typically favored. γ-Al_2O_3 is weaker acidic compared to zeolites, is a cheaper commercial most commonly used support [28] and will hence be used in this study. Basic catalysts tend to deactivate under deoxygenation conditions due to their strong tendency to react with acidic CO_2 and form stable/inert carbonates.

This work evaluates the in-line hydro-treatment of the bio-oil vapor generated from fast pyrolysis of biomass (termed as hydro-pyrolysis of biomass) over γ-Al_2O_3 supported Mo_2C and WC based catalysts. Generally, fast pyrolysis of biomass is performed at atmospheric pressure and high temperature, the in-line hydro-treatment of the pyrolysis bio-oil vapor investigated in the submission was thus carried out at the pyrolysis conditions. The catalyst performance was also compared with that of Pt/γ-Al_2O_3 catalysts.

2   Experimental

2.1   Catalysts preparation

γ-Al_2O_3 supported Pt, Mo_2C and WC catalysts were prepared by the wet impregnation method. $H_2PtCl_6 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ or $(NH_4)_6W_{12}O_{39} \cdot xH_2O$ were used as precursors for the corresponding catalysts. After impregnation, samples were dried at 105 °C and calcined at 500 °C. The calcined samples were further either (i) reduced under H_2 at 500 °C to form Pt/Al_2O_3 catalysts or (ii) carburized under 20 vol-% CH_4/H_2 at 650 °C followed by passivation under N_2 at 25 °C to form Mo_2C/Al_2O_3 and WC/Al_2O_3 catalysts. The catalysts are named as Ptx/Al_2O_3, Mo_2C-y/Al_2O_3 and WC-z/Al_2O_3, where x, y and z refer to Pt, Mo_2C and WC weight percentage loadings.

2.2   Catalysts characterization

The loadings of Pt or carbides on the catalysts were determined by Philips XRF spectrometer PW1480 which

was pre-calibrated. Surface area of the catalysts was measured by using Brunauer-Emmett-Teller (BET) method on Micrometrics Tristar 3000 instrument. The samples were degassed at 300 °C for 24 h prior the analysis. Scanning micrographs were taken on Zeiss MERLIN HR-SEM. Powder x-ray diffraction was recorded on a Bruker D2 Phaser diffractometer using CuK_{α} radiation at 40 kV and 40 mA. The diffraction pattern over the range between 10° and 90° was recorded.

2.3 Hydro-pyrolysis of biomass

Fast pyrolysis of biomass (Canadian pinewood, 0.5 mg) was performed under He (15 mL·min^{-1}) at 500 °C (~350 °C·s^{-1} heating rate) and atmospheric pressure on a Pyroprobe® 5200 pyrolyzer (ID = 1.5 mm, CDS Analytical, USA, Fig. 2). The produced fast pyrolysis bio-oil vapor was led for hydro-treating over the as-prepared catalysts (3 mg) at 500 °C in an in-line catalytic reactor (ID = 1.5 mm). The upgraded bio-oil by hydro-treatment (termed as HDO bio-oil) was analyzed on an on-line GC-MS (6890N-5975, Agilent, USA) system. Each reaction was performed two times to check the experimental reproducibility.

3 Results and discussions

3.1 Catalyst characterizations

Table 1 below shows the characteristics of the catalysts used in this study. BET surface area of the support is not affected at all by Pt loading, and only to a small extent by molybdenum carbide presence. The tungsten carbide catalysts had lower surface areas. XRF analysis (Table 1) showed that the loadings for (i) the Pt catalyst is 1.0 wt-% Pt, (ii) 10.1 and 19.6 wt-% Mo_2C for molybdenum carbide catalysts and (iii) 9.9 and 30.0 wt-% WC for tungsten carbide catalysts.

SEM micrographs of the catalysts are shown in Fig. 3 below. Looking at the textural characteristics of the samples, it can be seen that γ-Al_2O_3 consists of needle like grains. Incorporation of Pt does not seem to affect this textural characteristic. In excellent agreement, the BET surface areas of the two materials were quite similar (Table 1). Further, it can be seen that incorporation of Mo_2C changes shape of γ-Al_2O_3 grains only slightly. Correspondingly incorporation of Mo_2C changes surface areas of γ-Al_2O_3 only to a small extent. Presence of WC seems to have more influence on the texture of γ-Al_2O_3 and this is indeed seen in the BET surface area of the catalysts. What can further be concluded from these is that all the
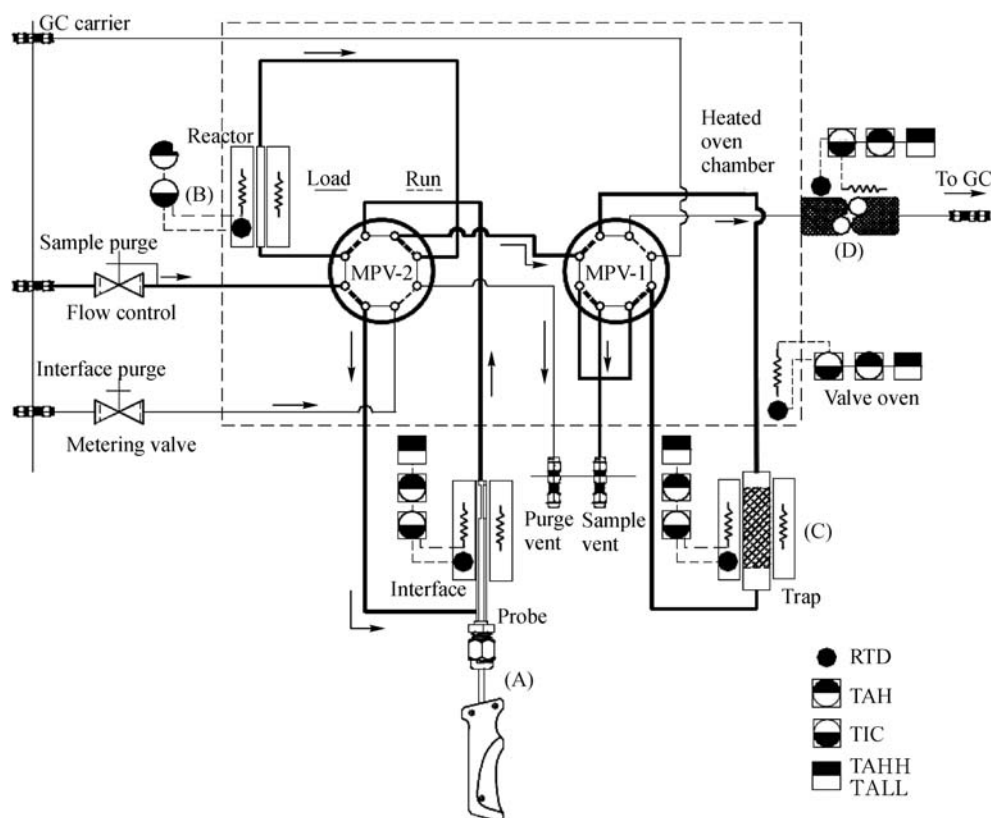

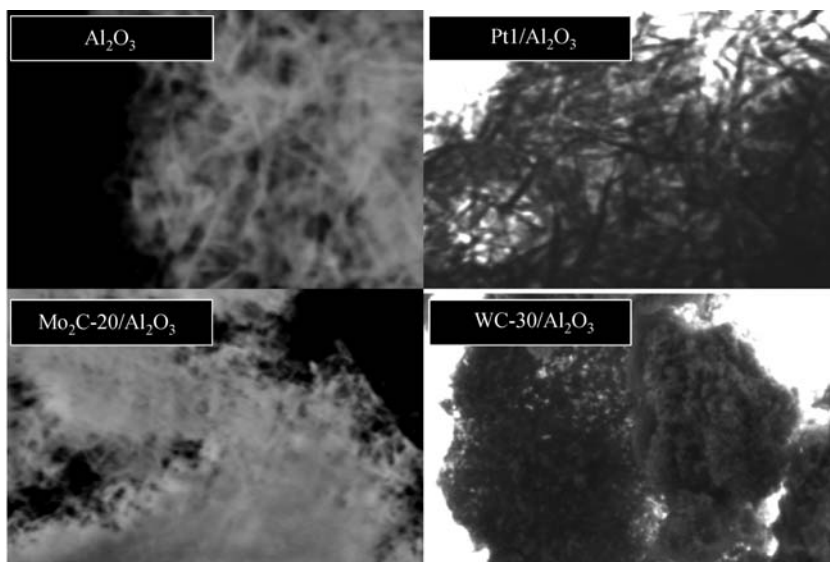**Fig. 2** Pneumatics of pyro-probe/GC-MS setup

Fig. 3   SEM morphologies of Al_2O_3 and the supported catalysts

Table 1   Characterizations of catalysts

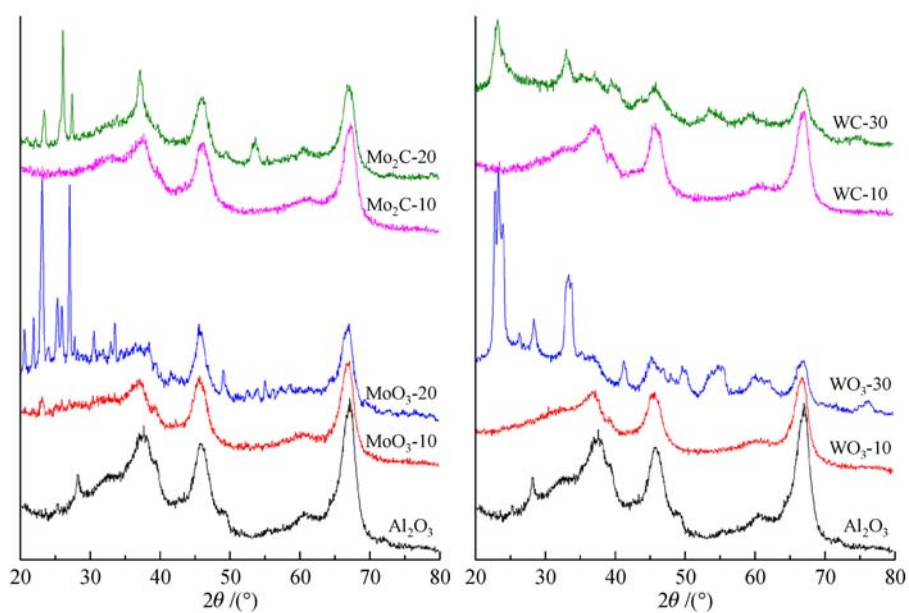|	S_{BET} /(m^2·g^{-1})	Loading /wt-%	Calculated carbide loading /wt-%
Al_2O_3	166	–	–
Pt/Al_2O_3	163	1.0[a]	–
WO_3-10/Al_2O_3	118	11.7[b]	9.9
WO_3-30/Al_2O_3	98	35.5[b]	30.0
MoO_3-10/Al_2O_3	151	14.1[c]	10.1
MoO_3-20/Al_2O_3	135	27.2[c]	19.6

a: Pt; b: WO_3; c: MoO_3

Fig. 4   XRD patterns of Al_2O_3 and the supported catalysts

catalysts can still have the acidic properties of γ-Al$_2$O$_3$ which can catalyze de-oxygenation.

XRD was used to identify the phases present on the catalysts and the XRD patterns are shown in Fig. 4 together with those of γ-Al$_2$O$_3$, molybdenum and tungsten oxides. Three typical and characteristic peaks of γ-Al$_2$O$_3$ can be seen in Fig. 4. Further, XRD of the two catalysts before carburization, e.g., containing molybdenum oxide formed during calcination, three peaks are seen at 23.6°, 25.7° and 27.4°. XRD reference data indicate that three main peaks are used to assign for the presence of molybdenum oxide. XRD database indicates that the most important peeks of molybdenum carbide are located at 35°, 38°, and 39°. The XRD reference data indicates that molybdenum carbide is present in hexagonal closed packed structure [10]. The lines in the diffractogram correspond to (100), (002), (101) facets of the crystal. This molybdenum carbide is present in β-phase. β-Phase crystals are hexagonal closed packed. The peaks of the Mo$_2$C-1 are small compared to peaks of MoO$_3$ 10 wt-% catalyst but the peaks of Mo$_2$C-2 are clearly visible in 20% catalyst and confirm that the carbide has been formed. Literature shows that WC should show typical peaks at 32°, 35° and 48°. Only at 32° a peak is visible that might be from WC, however this peak is also visible in the spectrum of WO$_3$. There is also a peak at 22°, which is typical for WO$_3$. From these spectra it can only be concluded that there is still WO$_3$ present on the carburized catalyst. There might be WC present on the catalysts, but this is maybe in highly dispersed smaller crystallites.

3.2   Performance of alumina supported Pt, Mo$_2$C, and WC catalysts

Product distributions of pyrolysis bio-oil obtained during experiments (i) in helium (DO) and (ii) in hydrogen (HDO), without or with catalysts (Al$_2$O$_3$ and the supported Pt, Mo$_2$C, and WC catalysts) are shown in Figs. 5 and 6. For the sake of simplicity, product oxygenates present in the bio-oil are grouped based on their chemical function-alities. In the absence of catalysts and He (Fig. 5, DO without catalysts), clearly, most of biomass was converted into carbonyls (72%, majorly coming from cellulose), phenols (20%, majorly from lignin) and small amount of acids (acetic acid, from cellulose) during the fast pyrolysis. Only marginal changes on the product distribution can be seen after the hydro-treatment without catalyst (Fig. 5, HDO without catalysts) being present. Interestingly, in the presence of hydrogen, acids are completely removed. When γ-Al$_2$O$_3$ was used in presence of hydrogen (Fig. 5, HDO over Al$_2$O$_3$), already significant changes in the product pattern was observed. Significant decrease in carbonyls, phenols and a corresponding increase in furans, aliphatic/aromatic hydrocarbons are observed. Acidity of γ-Al$_2$O$_3$ influences deoxygenation, especially via dehy-dration resulting in hydrocarbons.

Figure 5 also shows results over three Pt catalysts. As expected, in presnce of hydrogen, over Pt/γ-Al$_2$O$_3$ catalyst, further lowering of carbonyls is observed. Significant reduction in phenols is also obtained. Further, almost 60% of (aliphatic and aromatic) hydrocarbons are formed, which are as good as the reported performance over HDO catalysts (Pt, Rh, NiMo, etc.) [29,30]. This shows the effectiveness of Pt catalyst for hydro-treatment of the pyrolysis bio-oil vapor even under the pyrolysis conditions (high temperature and atmpspheric pressure), which are nor favorable for the hydro-treatment.

Figure 6 shows the results HDO experiments with pine wood over the carbide catalysts made in this study. In terms of reduction in harmful oxygenates (carbonyls, phenols) and required components (aliphatic, aromatic hydrocar-bons) the carbide catalysts perform very well. Compared to DO experiments (Fig. 5, DO without catalysts), carbonyls, which are harmful for the stability of the oil, are reduced drastically. Carbonyl content of the pyrolysis bio-oil for the DO experiment was about 73% (Fig. 5, DO without catalysts) and is lowered to 18% (Mo$_2$C-20/γ-Al$_2$O$_3$) and 38% (WC-10/γ-Al$_2$O$_3$) as shown in Fig. 6. The results are similar to those obtained over Pt catalysts.
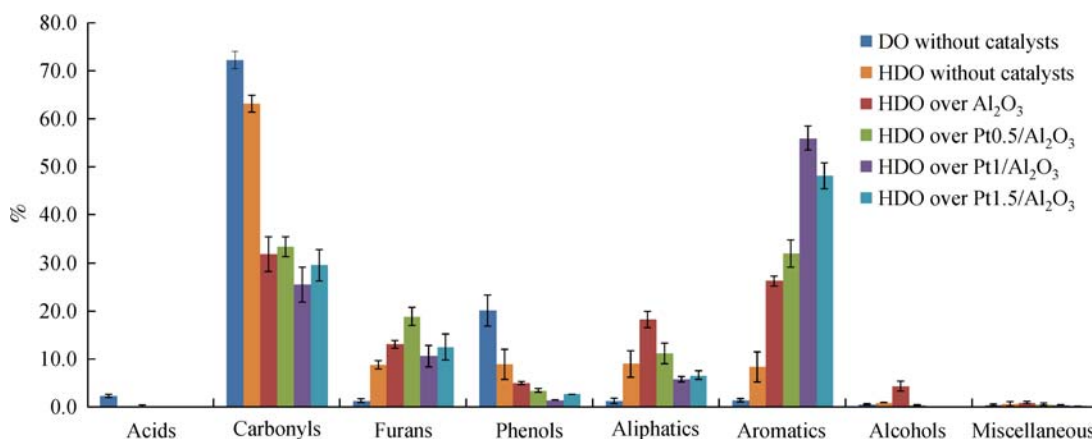

Fig. 5   Product distribution of HDO of fast pyrolysis oil over Pt/Al$_2$O$_3$ catalysts
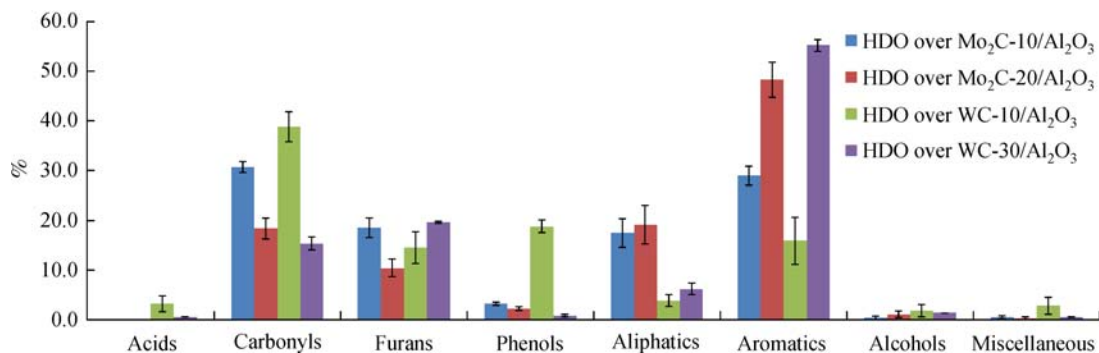
Fig. 6 Product distribution of HDO of fast pyrolysis oil over Al_2O_3 supported carbide catalysts
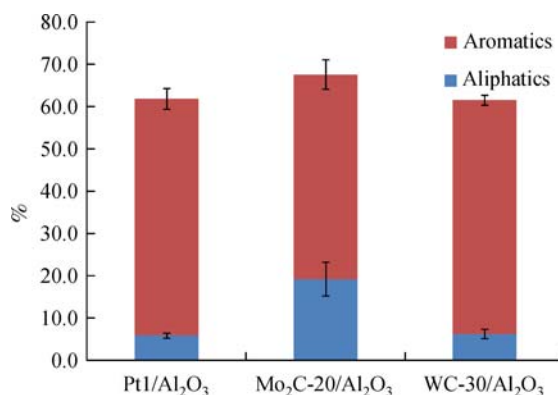

Fig. 7 Comparison of hydrocarbons formation over Al_2O_3 supported Pt and carbide catalysts

Over the carbide catalysts, higher amounts of hydrocarbons in the HDO bio-oil (Fig. 6) are observed compared to DO experiments (Fig. 5). Figure 7 compares the results obtained over Pt and carbide catalysts with reference to the formation of hydrocarbons, the key products while considering fuel applications. Interestingly, in comparison to Pt/γ-Al_2O_3 catalyst (60% hydrocarbons), Mo_2C-$20/\gamma$-Al_2O_3 catalyt gives 67.5% hydrocarbons and WC-$30/\gamma$-Al_2O_3 60% hydrocarbons. Thus the performance of the carbide catalysts are on par with Pt based catalysts. Further, Mo_2C-$20/\gamma$-Al_2O_3 catalyt yields 7% more hydrocarbons. Results shown in Fig. 7 further shows that over Mo_2C/γ-Al_2O_3 catalyst even more amounts of aliphatic hydrocarbons, ideally suited for fossil fuels blending, are formed compared to Pt or WC catalysts. This catalyst thus provides the most promise.

The production of acids for Mo_2C-$20/\gamma$-Al_2O_3 catalyt and $Pt1/\gamma$-Al_2O_3 catalyt is 0.0 wt-%. This is a good result because acids can cause corrosion problems [2]. The carbonyl production of Mo_2C-$20/\gamma$-Al_2O_3 catalyt is 18.4% and the carbonyl production of $Pt1/\gamma$-Al_2O_3 catalyt is 25.6%. This result shows that Mo_2C-$20/\gamma$-Al_2O_3 catalyt has good activity compared to $Pt1/\gamma$-Al_2O_3 catalyt and converts 7.2% more carbonyls than $Pt1/\gamma$-Al_2O_3 catalyt. The furan production of Mo_2C-$20/\gamma$-Al_2O_3 catalyt is 10.4% and the furan production of $Pt1/\gamma$-Al_2O_3 catalyt is 10.6%.

The Phenol production of Mo_2C-$20/\gamma$-Al_2O_3 catalyt is 2.3% and 1.5% for $Pt1/\gamma$-Al_2O_3 catalyt. This indicates that both catalysts are good at converting phenols into hydrocarbons. The key result in all these is that the total hydrocarbons production of Mo_2C-$20/\gamma$-Al_2O_3 catalyt consists of 19.2% aliphatic and 48.3% aromatic hydrocarbons. The total hydrocarbon production of $Pt1/\gamma$-Al_2O_3 catalyt consists of 5.8% aliphatic and 55.9% aromatic hydrocarbons. These results show that Mo_2C-$20/\gamma$-Al_2O_3 catalyt yields the highest yield of aliphatic hydrocarbons which is excellent because these compounds generally have a higher HHV as aromatic compounds.

4 Conclusions

This study explored the possibility of using carbide catalysts as substitutes for the expensive and scarce noble metal catalysts for in-line upgrading of the bio-oil vapor from fast pyrolysis of biomass. Results indicate that the hydro-treatment of bio-oil vapor over the noble and non-nobel metal catalysts under the pyrolysis conditions can controvert the acids and carbonyls to hydrocarbons (ca. 60%), indicating the efficiency of the hydro-treatment at high temperature and atmospheric pressure. The supported carbide catalysts, especially Mo_2C/γ-Al_2O_3

catalysts, are effective in hydrodeoxygenation as well as deeper hydrogenation to result in more aliphatic hydrocarbons, ideal fossil fuel components. Optimisation of this catalyst can lead to further exciting possibilities.

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