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Communication

Optimising the sustainability of crude bio-oil via reforming to hydrogen and valuable by-product carbon nanotubes

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Maximizing the efficiency and economic benefits of bio-oil is a major challenge for the emerging bio-refining industry. This research has developed a promising route to produce clean-fuel hydrogen with high value CNTs as a by-product via evaporation/pyrolysis-reforming of crude bio-oil. Since the waste catalyst coke is replaced by high-value CNTs, more than a significant potential increase of additional economic benefits could be contributed to the bio-refining process. Moreover, CO_2 emission to the environment from coke oxidation during catalyst regeneration would be reduced.

Introduction

Biomass has been regarded as a key renewable feedstock for a step change in the energy use in the UK,[1] to meet EU energy sustainability targets with at least 80% reduction of greenhouse gases towards 2050 compared with 1990 levels.[2] Many methods have been developed to transfer biomass to renewable fuels, such as gasification, pyrolysis, and hydro-thermal liquification. Among them, pyrolysis of biomass has been commercially developed and the product bio-oil has increased energy density compared with raw biomass.[3] However, this crude bio-oil cannot be directly utilized as tranportation fuel since it is an unstable, very complex mixture of hydrocarbons containing around 40% of oxygen, with low heating value, high moisture content and high viscosity.[4] Subsequent upgrading of bio-oil such as hydrodeoxygenation (HDO), catalytic cracking are requried to produce quality bio-fuels.[5-7] However, the high operation cost (hydrogen comsumption and expensive nobel metal catalysts) of the HDO process and the heavy coke formation during catalytic cracking has blocked further commercialisation.[6, 8 9]

One alternative method for the bio-oil upgrading is to produce clean fuel H_2 via the reforming of bio-oil.[10-12] Currently, aqueous and gas phase reforming are the two main routes. Aqueous phase reforming can produce H_2 with a low CO yield and low operation temperatures.[11, 13] However, the high operature pressure, low gas and hydrogen yield, and the high production of undesired CH_4 limit its wider application.[14] Gas phase reforming can combine with biomass pyrolysis to directly reform hot pyrolysis bio-oil vapour at aomosphere pressure without wasting energy by condensing the bio-oil after pyrolysis and re-vapourising the bio-oil before reforming. H_2-rich syn-gas is always obtained with high gas yield during gas phase reforming. However, one serious challenge for gas phase catalytic reforming is coke generation, which is derived from cracking of non-saturated, large molecular weight compounds in the crude bio-oil. The production of coke and CO_2 (regeneration of coked catalyst via calcination) from organic carbons in the crude bio-oil largely reduce the overall efficiency and promote greenhouse gas release. Therefore, developing a process that fully utilises the organic carbons is crucial for the sustainable development of biorefining based on biomass feedstocks. Here, we bring forward a method aimed to fully utilise the organic hydrogen and carbon resource from gas reforming of crude bio-oil.

Recently, carbon nanotubes (CNTs) with special physical properties and broad applications [15] have been successfully produced as a by-product during hydrogen production from pyrolysis/gasification of waste plastics and artificial biogas.[16-18] Therefore, the challenge here is to produce valuable CNTs instead of waste catalyst coke as a by-product in the gas phase reforming of bio-oils. The success of this research will dramatically increase the utilisation of organic carbons present in the oil, thus increasing the overall efficiency of the bio-refining process.

In this work, crude bio-oil was evaporated or pyrolysed initially in a reactor to retain solid particles and heavily polymerized hydrocarbons (within crude bio-oil). In the second gas phase reforming of crude bio-oil, high-value CNTs was targeted as a high value by-product of the hydrogen production process instead of problematic catalyst coke production.

Experimental

A two-stage reaction systme was used for reforming of crude bi-oil. Around 3 g of crude bio-oil (derived from wood pyrolysis) was placed in the sample boat located in the first reactor. 0.5 g Ni-based catalyst was placed in the second reactor. The catalytic reactor (second reactor) was heated under N_2 flow (80 ml min^{-1}) at 800 ºC. When the catalytic temperature was stabilised, the first reactor was started to be heated to the set temperature e.g. 500 ºC for evaporation/pyrolysis. The derived gaseous products were reformed in the second reactor in the presence/absence of catalyst. Non-condensed hydrogen was collected with a gas sample bag with other gases e.g. N_2, CO and CO_2. The carbon materials were produced on the surface of the catalyst. Total reaction time was around 80 min.

The catalysts were prepared by a co-precipitation method with an initial Ni-loading mole ratio of 5, 20 or 35 mol.%.

$Ni(NO_3)_3·6H_2O$ (≥97.0%), $Ca(NO_3)_2·4H_2O$ (≥99%), $Al(NO_3)_3·9H_2O$ (≥99%), and NH_4OH (≥98%) were purchased from Sigma–Aldrich. Precursors with the desired Ni-Ca-Al (Ca/Al molar ratio 1:1) and Ni content were precipitated with a basic solution of NH_4OH drop by drop in order to adjust the pH of the suspension between around 8. After precipitation, the suspension was aged under agitation for an hour and then filtered under vacuum, followed by drying at 80 °C overnight. The solid products were calcined at 800 °C for 4 h with a heating rate of 1 °C min^{-1} in static air.

The non-condensed gases were analysis by Varian 3380 gas chromatograph. The catalysts were characterised by X-ray diffraction (XRD) (Bruker D8), a scanning electron microscopy (SEM) (LEO 1530), a transmission electron microscopy (TEM) (FEI Tecnai TF20) and a Raman spectroscopy (Renishaw Invia) at a wavelength of 514 nm at Raman shifts between 100 and 3200 cm^{-1}.Temperature program oxidation (TPO) has also been used to obtain the information of coke formation on the reacted using a thermogravimetric analyser (TGA) (Shimazu).

Results and discussion

The CNTs production and influence of process conditions are investigated here by using two-stage evaporation/pyrolysis-reforming of crude bio-oil (schematic diagram of reaction system is shown in Fig. S1). The presence of catalyst was crucial to produce and manipulate the targeted products during the reforming of crude bio-oil. Currently, Ni-based catalysts have been widely utilized in catatlytic reforming due to the relative low cost.[5, 19] In the present research, NiCaAl catalyst prepared by co-precipitation was firstly tested for producing both hydrogen and CNTs from the reforming process.[16]

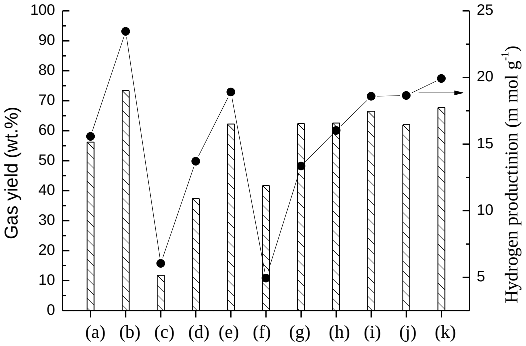

Fig. 1. Gas yield and hydrogen production from the catalytic reforming of crude bio-oil. Vaporization/pyrolysis temperature: 500 ˚C for (a) (b) (f) (g) (h) and (i), 100 ˚C for (c), 180 ˚C for (d), 230 ˚C for (e), 100+180+230+500 ˚C for (j) and 100+500 ˚C for (k). Reforming temperature: 700 ˚C for (a), 900 ˚C for (b) and 800 ˚C for other experiments. Catalyst bed: 20NiCaAl for (a) (b) (c) (d) (e) (h) (j) and (k), sand for (f), 5 NiCaAl for (g), 35 NiCaAl for (i).

The hydrogen and gas productions during the reforming of crude bio-oil at 800 ˚C on 20NiCaAl catalyst were clearly increased, from 6.0 to 18.9 mmol g^{-1} bio-oil and 11.8 to 62.4 wt.%, respectivly, with the increase of the fist-stage evaporation/pyrolysis temperature from 100 to 230 ˚C (Fig.1 (c) and (e)). Further increasing evaporation/pyrolysis temperature to 500 ˚C, showed that hydrogen production (16.0 mmol g^{-1} bio-oil) was a little decreased and gas yield (62.6 wt.%) was only increased slightly as shown in Fig. 1(h) after the second-stage catalytic reforming. A slight increase of gas and hydrogen production was observed (e.g. gas yield increased from 62.7 to 67.7%), when crude bio-oil was evaporated/pyrolysed at a final temperature of 500 ˚C with different heating programmes (Fig.1 (h), (j) and (k)).

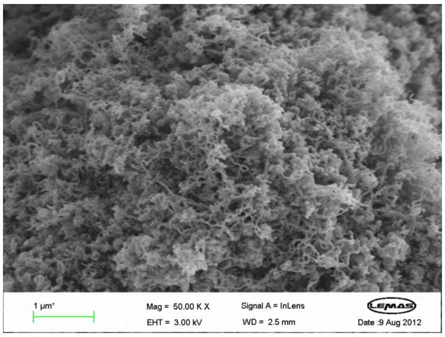

Fig. 2. SEM result of the reacted 20NiCaAl catalyst after crude bio-oil reforming. Nano-filamentous carbons were clearly observed.

Adding Ni catalyst has significantly improved the hydrogen production from 4.9 (on reference sand) to 13.4 mmol g^{-1} bio-oil on 5NiCaAl. Further increasing Ni loading from 5NiCaAl to 20NiCaAl and 35NiCaAl, the hydrogen production was increased from 13.4 to 16.0 and 18.6 mmol g^{-1} bio-oil, under the evaporation/pyrolysis temperature and reforming temperature of 500 and 800 ˚C, respectively (Fig. 1 (g), (h), and (i)). Among the catalysts with different Ni loadings, the reforming on 20NiCaAl generated the gas with the highest H_2 concentration (48.2 Vol.%, N_2 free) as shown in Table S1.

The scanning electron microscopy (SEM) analysis of the used catalysts showed that more carbon filaments were produced on the reacted 20NiCaAl catalyst (Fig. 2) compared with that on the reacted 5NiCaAl and 35 NiCaAl catalysts (Fig. S2). Further investigation by transmission electron microscopy (TEM) confirmed that CNTs were produced after the reforming of crude bio-oil as shown in Fig. 3. The orientatino of graphene sheets are mostly parallel to the axis of the CNTs.

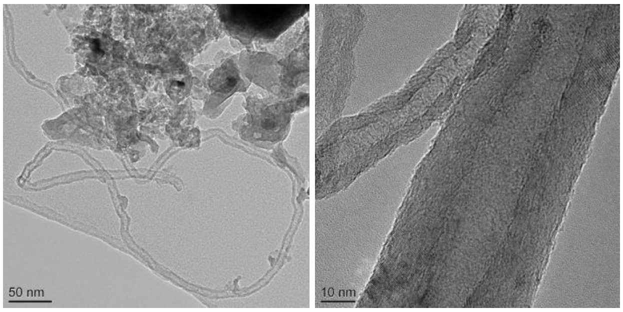

Fig. 3. TEM analysis of the reacted catalyst. CNTs were confirmed as product carbon nano-materials from reforming of crude bio-oil at evaporation/pyrolysis temperature of 500 ºC and reforming temperature of 800 ºC with the 20NiCaAl catalyst.

Raman spectroscopy was used to characterize the graphitization of the CNTs (Fig. 4). The peak at around 1350 cm^{-1} (D band) which corresponds to disordered amorphous carbons and the peak around 1575 cm^{-1} (G band) is assigned to tangential vibrations of the graphite carbons (i.e. crystallinity).[20] A relative low ratio of intensity of the D to G bands (0.66) was obtained in this work compared with literature[17, 21] and one commercial CNTs obtained from Chendu Organic Chemicals. In addition to the high intensity of the G’ band at around 2690 cm^{-1} (related to high purity CNTs[20]), indicating highly crystalized CNTs have been obtained from catalytic reforming of crude bio-oil.

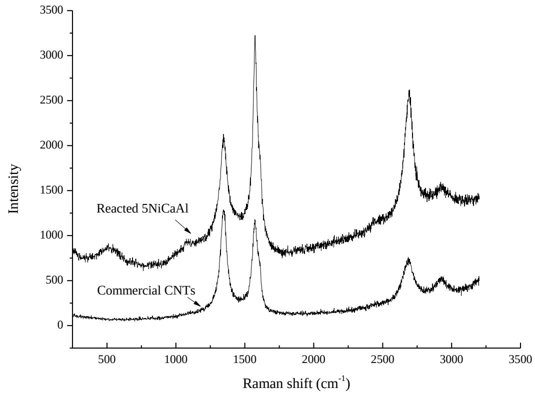

Fig. 4. Raman analysis of carbons deposited on the reacted 5NiCaAl catalyst at evaporation/pyrolysis temperature of 500 °C, reforming temperature of 800 °C, 5NiCaAl catalyst, and commercial CNTs

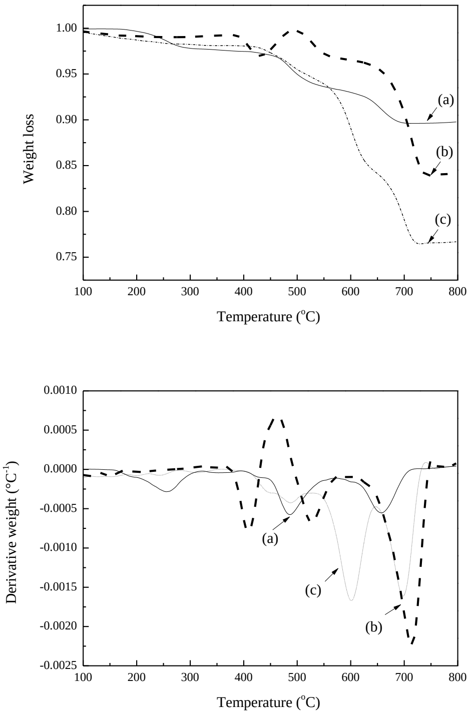

Fig. 5. Temperature program oxidation (TPO) of deposited carbons on reacted catalysts; Top- thermogravimetric analysis (TGA), Bottom-Derivative thermogravimetric (DTG) at evaporation/pyrolysis temperature of 500 °C, reforming temperature of 800 °C; (a) 5NiCaAl, (b) 20NiCaAl, (c) 35NiCaAl.

Oxidation of the deposited carbons on the reacted catalysts with different Ni loading was conducted by temperature program oxidation (TPO). From the TPO-TGA results shown in Fig. 5, more than 20 wt.% of the weight of catalyst was obtained as deposited carbons after the reforming of 3 g of crude bio-oil. Various types of carbons seem to be produced, as several oxidation peaks were observed from the TPO-DTG results (Fig. 5). Oxidation peaks of TPO-DTG before 550 ˚C could be assigned to amorphous carbons and after 550 ˚C could be ascribed to filamentous carbons.[22, 23] Both types of carbons are found from the TPO-DTG analysis; however, the filamentous carbon is the major product. The Ni loading has shown a strong influence on the TPO results. A major single oxidation peak was observed around 710 ˚C for the reacted 20NiCaAl catalyst; while two major oxidation peaks were found after 500 ˚C for the reacted 35NiCaAl catalyst (Fig. 5). Oxidation of filamentous carbons after 550 ˚C by TPO analysis were proposed to be mainly carbon nanotubes detected from the TEM analysis (Fig. 3).

However, only filamentous carbons seem to be obtained (with a single oxidation peak) from TPO analysis of the reacted 20NiCaAl catalysts (Fig. S3) (further confirmed from SEM analysis, Fig. S4), when the first-stage evaporation/pyrolysis temperature was controlled at 100 or 180 ˚C (the results of gas production shown in Fig. 1(c) and (d)). Obviously, lower evaporation/pyrolysis temperature will promote CNTs production in the second-stage reforming. While, higher evaporation/pyrolysis temperature is suggested to be favourable for the prodction of amorphous carbons or heavy hydrocabrons as by-products at the second catalytic reforming stage.

Therefore, an optimal evaporation/pyrolysis temperature for crude bio-oil reforming could be selected thereby enabling the tuning of hydrogen production or CNTs production according to the chemical/materials markets. A higher evaporation/pyrolysis temperature could be required to generate more hydrogen for the fast-developing clean-fuel market; while a lower evaporation/pyrolysis temperature could produce higher purity CNTs with enhanced economic benefits. In the reaction system presented in this research, crude bio-oil could also undergo lower temperature evaporation/pyrolysis for CNTs production at first, and then switch into higher temperature for hydrogen production (Fig. 1(j) and 1(k)). Clearly, flexibly combining hydrogen and CNTs production via simple operation parameters will significantly improve the commercial development of bio-oil reforming.

Reforming temperature (700, 800 and 900 ˚C) of the crude bio-oil was also studied in the presence of the 20NiCaAl catalyst. However, no obvious influence was obtained on the amount of deposited carbons (TPO results shown in Fig. S5); although hydrogen and gas yield were expected to be increased with the increase of the reforming temperature (Fig. 1 (a)(h)(b)) due to the endothermic reforming reactions which were favoured at higher temperature.

Conclusions

In summary, this preliminary investigation provides a potential solution to maximize process efficiency and sustainability of using renewable energy resources. With the production of clean hydrogen and high-value by-product CNTs, organic carbons in the crude bio-oil were mostly utilised rather than combused to CO$_2$ via the calcination of the coked catalysts. Both CNT’s and hydrogen are valueable commodities,[24, 25] therefore, in addition to hydrogen production, economic value will be added by replacing the production of catalyst coke by CNTs during the reforming of crude bio-oil. In addition, a reduction of CO$_2$ from catalyst regeneration would be realised. The quality and yield of CNTs and hydrogen could be well controlled by tuning operation parameters and Ni loading on catalysts. This allows the plant operators to flexibly adjust product selectivity during reforming according to the market values of the CNTs and hydrogen. By maximizing the process efficiency in terms of carbon utilisation, the new utilization route of crude bio-oil presented in this research significantly improves commercialization in terms of economic, environmental and technical issues.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Schematic diagram of process, mass balance, gas concentrations and additional SEM, TPO analysis. See DOI: 10.1039/b000000x/

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