



Research article

In situ performance of various metal doped catalysts in micro-pyrolysis and continuous fast pyrolysis



Güray Yildiz^{a,*}, Frederik Ronsse^a, Jop Vercruyssen^a, Jalle Daels^a, Hilal Ezgi Toraman^b, Kevin M. van Geem^b, Guy B. Marin^b, Ruben van Duren^c, Wolter Prins^a

^a Department of Biosystems Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium

^b Laboratory for Chemical Technology (LCT), Ghent University, Technologiepark 918, B-9052 Ghent, Belgium

^c Albemarle Catalysts Company BV, Nieuwendammerkade 1-3, P.O. Box 37650, 1030 BE Amsterdam, The Netherlands

ARTICLE INFO

Article history:

Received 24 September 2015

Received in revised form 18 December 2015

Accepted 11 January 2016

Available online 27 January 2016

Keywords:

Bio-oil

Catalytic fast pyrolysis

Pine wood

Auger reactor

Heterogeneous catalysis

Py-GC/MS

ABSTRACT

Catalytic fast pyrolysis (CFP) of biomass is a promising route for the production of deoxygenated liquids suitable for further conversion to fuels and/or chemicals. In this work, CFP of pine wood in a micro-pyrolysis setup and a continuously operated bench-scale fast pyrolysis unit was performed to investigate the effect of catalyst type and reactor type on the products. In total, eight zeolite catalysts (metal doped acidic, basic, and γ -alumina catalysts and their parent counterparts) were tested. In the bench-scale unit, the distribution of products including liquid organics (i.e. CFP-oil), water, char, coke, and non-condensable gases (NCGs) were measured, as well as the compositions of the CFP-oil and NCGs. CFP gives rise to the production of additional water, coke, and NCGs at the expense of CFP-oil. However, the quality of the obtained CFP-oil was altered significantly depending on the catalyst type. For all catalysts, the acidity of CFP-oils remarkably decreased with an increased deoxygenation. The best performance was obtained with the lower redox-metal containing acidic catalyst and freshly calcined metal doped basic mixed-metal oxide catalysts. Py-GC/MS results obtained with the same catalysts were found to be only partially indicative for the performance of a catalyst in CFP of biomass.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Lignocellulosic biomass is a renewable resource providing an alternative to fossil fuels. It has also the potential to sustain the chemical economy, which is currently largely petroleum-based. Fast pyrolysis of biomass is emerging as a cost effective thermochemical conversion technique that can yield a liquid product (i.e. pyrolysis liquid, bio-oil) in high quantities. When the target is to use the pyrolysis liquids in replacing the petroleum fuels its quality needs to be improved. As most of the crude bio-oil's adverse properties are caused by its highly oxygenated nature, bio-oil improvement basically refers to a reduction in the oxygen content (deoxygenation). For this purpose catalytic fast pyrolysis (CFP), which is a single step process that uses heterogeneous catalysts reacting with biomass derived pyrolysis vapours at atmospheric pressure [1–3], can be put in service.

The possibility to feed a deoxygenated pyrolysis liquid into the existing petroleum refinery infrastructure (i.e. blending with vacuum gas oil (VGO) prior to the FCC) would make CFP an attractive route for biomass conversion [4]. The presence of the catalysts in CFP induces reactions that involve the removal of the oxygenated species and enhance

the cracking reactions of the heavy molecules in primary pyrolysis vapours. With the use of different catalysts, varying degrees of deoxygenation can be achieved via simultaneous decarbonylation (CO rejection), decarboxylation (CO₂ rejection) and dehydration (H₂O forming) reactions [5–7]. These reactions alleviate the high acidity, and the high viscosity of the pyrolysis liquid and increase its stability and calorific value.

In CFP of biomass, the type of the catalyst affects the mechanism of oxygen removal and the spectrum of the produced chemical compounds. The catalyst properties play a vital role in the selectivity towards higher value compounds (alkanes, phenolics, mono-aromatic hydrocarbons, etc.) while avoiding undesirable compounds (sugars, acids, poly-aromatic hydrocarbons, etc.) [8–10]. However, since each catalyst favours different reaction mechanisms, some specific chemicals (i.e. aromatics) cannot be produced with every catalyst. Indeed, selectivity can be tuned by changing the physical and/or chemical properties (surface area, pore size, impregnation of active metals, etc.) of the specified catalyst or by mixing different catalysts together. Hence, the targeted product specifications determine the selection of the catalyst that serves through the purpose of the CFP operation.

The reported research regarding the development of CFP of biomass spans a wide range of catalyst combinations, temperatures, and feedstocks in an effort to develop fundamental knowledge on the catalytic effects, processes and operating conditions. Apparently, the main goal

* Corresponding author.

E-mail addresses: guray.yildiz@ugent.be, guryildiz@gmail.com (G. Yildiz).

was to produce a liquid product with less oxygenated compounds and possibly richer in high-value compounds. A large number of studies in the CFP literature have focused on maximizing the production of aromatic hydrocarbons [11]. However, the production of aromatics should not be the only criterion that values a catalyst in CFP conditions. Deoxygenation capability, removal of reactive oxygen functionalities, the ability to suppress the formation of coke and PAHs, the activity and lifetime of the catalyst are other parameters that should be considered carefully.

The main objective of this study was to find the best performing catalysts capable of retaining the amount of the organic liquid products as much as possible with a minimum water production, and also achieving an effective reduction of the acidity during in situ CFP of pine wood. In order to determine their individual cracking and deoxygenation performances in in situ fast pyrolysis of pine wood, eight proprietary zeolite catalysts supplied by Albemarle Catalyst Company B.V. (Amsterdam, The Netherlands) were tested. Both a py-GC/MS system and a continuously operated mini-plant based on auger reactor technology were used while applying the same temperature (500 °C) and catalyst-to-biomass ratio (5). Based on the type of the carrier, their acidity (acidic and basic catalysts), the active metal they contain, and according to the aged/freshly calcined distinction, these catalysts were divided into three groups. The experimental results obtained from in situ application of the catalysts were compared to each other and to the results of non-catalytic experiments which were designated as the base case. The results obtained from the continuously operated bench scale mini-plant were investigated based on the product yields (organics, water, char, coke and non-condensable gases), elemental compositions of these product fractions, the acidity and the composition of the pyrolysis liquids (via a GC × GC/MS). The results obtained from py-GC/MS experiments and the use and validity of py-GC/MS in CFP research has been investigated as well. By the comparison of the performances of a range of catalysts in a bench-scale pyrolysis reactor and a micropyrolysis system – as the latter system is commonly used to assess the performance of a catalyst in biomass pyrolysis in a quick way (i.e. in screening) – the objective is to verify whether catalyst performance on a larger scale reactor is similar to or deviating from the one observed in pyGC and whether this is dependent on the specific catalyst type. Deviation in catalyst behaviour between both reactor scales urges for careful interpretation and comparison of pyGC-based catalyst assessment data with those obtained in larger, continuous pyrolysis systems and could be a strong message relevant to the research community. Moreover, the suggested evaluation criteria and ranking of the performances of different catalysts (see Section 3.4 and Tables S.5a and S.5b) – which are rarely discussed in the existing literature – are provided.

2. Experimental section

2.1. Materials

2.1.1. Biomass feedstock

Pine wood (Bemap Houtmeel B.V. (Bemmel, Netherlands) was used as the reference biomass feedstock in all experiments. The number-average particle size of pine was between 1 and 2 mm. The moisture and ash content were determined to be 8.4 wt.% and 0.3 wt.% on a “as-received” basis (a.r.), respectively. For py-GC/MS experiments, the pine wood sample was finely ground in a centrifugal mill and screened to obtain samples with particle sizes of ca. 100 µm. The proximate analysis data, elemental composition, alkali metal content and HHV of the pine wood are listed in Table 1.

2.1.2. Catalysts

Eight proprietary catalysts were used to investigate their impact on pyrolysis product distribution. The catalysts supplied by Albemarle Catalysts Company B.V. (Amsterdam, The Netherlands) were provided in

Table 1
Properties of pine wood.

Proximate analysis (wt.%)	
Fixed carbon (d.b.)	15.0
Volatiles (d.b.) [ASTM E872-82]	84.8
Moisture (a.r.) [ASTM E871-82]	8.4
Ash (d.b.) [ASTM E1755-01]	0.3
Ultimate analysis (d.b.) [wt.%]	
C	47.1
H	5.9
O	46.4
N	0.04
S	0.06
Alkali metals (d.b.) [mg/kg]	
K	346
Na	10
Mg	113
Ca	767
HHV (a.r.) [MJ/kg] [†]	16.8
HHV (d.b.) [MJ/kg]	18.3

[†] Calculated by using the Milne formula [12].

powdered form. To minimize the water accumulation in the final liquid product, most catalysts were calcined in air at 500 °C for 1 h before shipment to decrease the catalyst bound/absorbed moisture content to below 1 wt.%, after which they have been packaged under inert conditions; with the exception of the catalysts labelled with the suffix “-A”, which had been calcined and subsequently stored for five months to study the effect of ageing on the catalyst. Here, the term ‘ageing’ represents the anticipated adsorption of water and/or CO₂ on the catalyst from its contact with air.

The first group of (three) catalysts are all based on an acidic zeolite (ZSM-5) containing material and have been labelled “A” for acidic. Two major catalyst variations were made, both containing a not-further-specified redox metal M1. The first modification, termed A-M1-H, contained a high amount of redox metal M1. The second modified version had a lower metal content and lower zeolite content. This catalyst has been labelled A-M1-L. The catalysts in this group contain varying amounts of ZSM-5 in their structure, viz. 40 wt.% in catalyst A and 28 wt.% in A-M1’s. The M1 metal content for the low metal version is more than five times lower than the high metal version. This variation in metal content had no measurable effect on the total surface area, but selective pore blocking cannot be excluded. As a result of the loading of redox metal M1 on the particles (typically 90 µm in diameter), the averaged diameter increased significantly for both “-H” and “-L” variants.

The three catalysts of Group 2 were based on the same basic material, denoted as “B”. Catalyst B is known for its hygroscopic nature and had a much higher loss-on-ignition (L.O.I.) compared to other catalyst after prolonged exposure to (moist) air. On this basic material B, the metal M2 has been added in a similar amount as M1-L. The obtained catalyst is named B-M2. As being the same catalyst, the difference between B-M2-A and B-M2-F is the aged and fresh distinction. After being synthesized, B-M2 was calcined and stored. After 5 months, half of the B-M2 was taken and calcined one more time and named as B-M2-F (fresh). The remaining aged part was then labelled as B-M2-A (aged). Due to the loading with metal M2, the (BET) surface area of the particles halved compared to the original B catalyst.

The last group of catalyst was prepared from a γ-alumina material and subsequently labelled as “G”. This catalyst also contained the metal M2 as used in the basic catalyst B-M2 in the same amount, and distinction was made between aged material G-M2-A and freshly calcined G-M2-F.

Prior to each mini-plant experiment, catalysts were blended with silica sand (PTB-Compaktuna, Gent, Belgium) with a mean diameter of 250 µm and a particle density of 2650 kg/m³ (compacted bulk density = 1660 kg/m³).

Download English Version:

<https://daneshyari.com/en/article/209288>

Download Persian Version:

<https://daneshyari.com/article/209288>

[Daneshyari.com](https://daneshyari.com)