Applied Catalysis B: Environmental 168 (2015) 203–211

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Effect of biomass ash in catalytic fast pyrolysis of pine wood

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ARTICLE INFO

Article history:
Received 11 September 2014
Received in revised form
19 December 2014
Accepted 23 December 2014
Available online 27 December 2014

Keywords:
Pine wood
ZSM-5
Ash
Catalytic fast pyrolysis
Catalyst regeneration

ABSTRACT

Fast pyrolysis experiments of pine wood have been performed in a continuously operated mechanically stirred bed reactor at 500 °C. The effects of the pine wood ash were studied by comparing non-catalytic and catalytic experiments (using a ZSM-5 based catalyst) with their ash-added counterparts. To show the case of ash accumulated from the biomass feeding, the results of catalytic fast pyrolysis obtained after eight reaction/catalyst regeneration cycles were included as well. The objective was to distinguish between the ash-catalyst interactions and the catalyst deactivation. The latter may be caused by thermo-mechanical, chemical and/or structural changes in the catalyst; such as poisoning, fouling, and attrition, as well as by coke deposition. Ash concentrations up to ca. 3 wt.% relative to the amount of pine wood fed, and ca. 0.002 wt.% relative to the amount of bed material, were found to be sufficient to change the distribution and the composition of pyrolysis products. The addition of ash to the catalytic fast pyrolysis, caused a reduction in the yields of both the organics and coke by 2 wt.% (on feed basis), while increases of 1 wt.% and 4 wt.% in the water and non-condensable gases were observed, respectively. The total yield of CO plus CO_2 was boosted by more than 10%, while the CO_2 production (decarboxylation reactions) was favoured clearly. Moreover, the presence of added-ash suppressed the conversion of sugars and acids – these were more pronounced in the case of accumulated-ash – as well as of the phenols. The catalyst deactivation during the reaction/regeneration cycles is not only related to the presence of ash but also to changes in the structure and composition of the catalyst. To overcome the drawbacks of biomass ash in catalytic fast pyrolysis, either the biomass feedstock has to be leached (ash removal) before being introduced to the process, or the char (which contains a vast majority of the biomass ash) has to be physically removed from the catalyst before the regeneration step.

1. Introduction

Lignocellulosic biomass is an abundantly available, renewable resource of organic carbon and can be transformed into energy-dense alternative liquid fuels through fast pyrolysis. Fast pyrolysis is the thermal decomposition of the natural polymeric constituents of biomass in an oxygen-free atmosphere at temperatures around 500 °C. At optimal conditions, including high heating rates of the biomass particles, short vapour residence times and fast condensation of pyrolysis vapours, high yields of pyrolysis liquid (usually in the range of 60 to 70 wt.%, dry-feed basis) can be achieved.

However, some adverse properties of pyrolysis liquid limit its use in chemicals production and fuel applications. These include its high water content (15–30%), oxygen content (35–40 wt.%), corrosiveness (pH of 2–3), relatively low heating value compared to fossil fuels (ca. 17 MJ/kg), poor volatility and high viscosity. Hence, the quality of pyrolysis liquids must be improved before they can be considered as a liquid feed in the production of heat, electricity, transportation fuels and chemicals [1]. Catalytic fast pyrolysis (CFP), which is based on the use of heterogeneous catalysts in the fast pyrolysis process, intends to improve the quality of the liquid by steering the vapour phase reactions with respect to rates and selectivity.

In a CFP process, the inert heat transfer material is (partially) replaced by a solid catalyst. The presence of catalyst favours oxygen removal via decarbonylation (CO rejection), decarboxylation (CO_2 rejection) and dehydration (H_2O formation) reactions. The

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http://dx.doi.org/10.1016/j.apcatb.2014.12.044
0926-3373/

ultimate composition of the produced liquids is influenced by factors such as the type of the biomass feedstock, the type of the catalyst (including pore size, acidity, nature of active sites and the presence of metals), optimal operating temperature of the catalyst, and the catalyst-to-feed ratio. In addition, the interaction between the volatiles generated by fast pyrolysis and the bed contents (e.g. catalyst, char, and ash) is an important feature of the pyrolysis reactor. More specifically, this interaction refers to reactions of reactive species present in the volatiles (including radicals generated by thermal cracking) with the char/ash particles [2]. Obviously, the selected catalyst should play a vital role in suppressing the production of undesirable oxygenated compounds (acids, sugars, poly-aromatic hydrocarbons, etc.) while promoting the production of value-added compounds (phenolics, alkanes, mono-aromatic hydrocarbons, etc.). Regarding the corresponding removal of oxygen, the preferred route from both, an energy-yield point of view and the desire to maintain a relatively high H/C ratio, must be decarboxylation [3,4].

One of the problems encountered in CFP is the deactivation of the catalyst which implies the physical, chemical, thermal, and mechanical degradation of the catalyst leading to a reduced activity and selectivity [5]. In CFP, deactivation mainly occurs by the deposition of coke and metals on the catalyst which can poison the active sites of zeolites or block the pores [6]. Accumulation of ash on or inside the catalyst could also be responsible for catalyst deactivation, as it is reported that biomass originated alkali and alkaline earth metals (AAEMs) can poison the catalyst [1]. Like in conventional FCC (fluid catalytic cracking) processing, the catalysts deactivated by coke can be reused in a CFP process after being regenerated. In FCC regeneration, the catalyst is subjected to high temperature oxidative treatment to burn the coke off from the catalyst and thereby (partially) restore its activity [7]. In biomass CFP however, the coke-on-catalyst contains more oxygen and hydrogen than the coke-on-catalyst obtained in FCC processing. Regeneration of the catalysts thus yields water, apart from only CO_x ($CO + CO_2$), which for ZSM-5 and similar structured catalysts could lead to dealumination, and thus, loss of active (acid) sites [6,8].

All biomass materials contain ash-forming mineral nutrients in the form of cations which are bound onto the organic matrix of biomass at carboxylic and/or phenolic groups, or in the form of precipitates, such as a salt [9]. These indigenous and catalytically active minerals included in the biomass structure, such as alkali and alkaline earth metals (AAEM species, e.g. Ca, K, Mg, and Na), are known to catalyse cracking and several thermolysis reactions in the vapour phase and remould the chemical composition of a resulting pyrolysis liquid, and change the pyrolysis product distribution [10–15].

To prevent their diverse effects on pyrolysis product quality and distribution, the ash-forming elements can be removed from the biomass to some extent by washing with water, and more extensively by using an acidic washing liquid [16]. The main chemical composition of biomass is sensitive to the leaching conditions wherein harsh leaching can cause the degradation of hemicellulose [13,17]. Leaching also influences the chemical composition of pyrolysis liquid [18]. Even very small quantities of either alkali or alkaline earth metals in their chloride forms were shown to be sufficient to significantly alter the pyrolysis products. The presence of as little as 0.5 wt.% ash led to a strikingly different chemical speciation: in terms of levoglucosan yield, the order of strong to modest influence was found to be $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ [11].

While the conclusions concerning the effects of inorganic minerals on non-catalytic pyrolysis are well known, only few literature studies are available regarding the effects of ash and its constituents on the CFP of biomass. As of today, various projects have tried/are trying to push catalytic fast pyrolysis to the pilot scale or even to the commercial scale and have met varying levels of success. Moreover, most of the studies in CFP literature concern the use of fresh catalyst; whereas, in large-scale practical applications, the spent (and coked) catalyst is regenerated (subjected to combustion) to be returned to the pyrolysis process [19]. Although, this is pretty much similar to the FCC process in an oil refinery, one aspect that is different – and thus, far not properly understood – is that biomass also contributes mineral matter (or ash) to the process. Through successive cycles of pyrolysis and catalyst regeneration, a considerable amount of this ash accumulates and could potentially affect the chemistry of pyrolysis as well as the stability and/or the activity of the catalyst. Mullen et al. [20] examined the accumulation of Ca, Cu, Fe, K, Mg, Na, and P from switchgrass on HZSM-5 during the catalytic pyrolysis in a fluidized bed reactor. The total amount of these elements was observed to be accumulated on HZSM-5 in a linear fashion during the successive use of the same catalyst sample. The catalytic activity, as measured by a drop in deoxygenation of the pyrolysis oil products and in selectivity of aromatic hydrocarbons, was decreased concurrent with the increase in inorganic elements on the HZSM-5. They concluded that some factors such as catalyst attrition could contribute to the decrease in catalytic activity, and the reactor designs decreasing the exposure of the raw biomass with the catalyst would be beneficial to catalyst lifetimes. Paasikallio et al. [21] performed the CFP of pine sawdust in VTT's Process Development Unit with a biomass throughput capacity of 20 kg h^{-1}. A spray dried HZSM-5 catalyst was used. The changes in product yields, physical and chemical properties of the CFP products, and the changes in the properties and the structure of the catalyst were observed during a continuous run of over four days. Coke formation on the catalyst was observed to be heaviest at the beginning of the experiment, but then subsided over time. Catalyst micropore area and volume also decreased during the experiment; these were accompanied by apparent changes in the crystallinity and the structure of the catalyst. Biomass alkali metals (e.g. Ca, K, Mg, P, etc.) deposited on the catalyst in time, and a linear correlation was observed between this phenomenon and the decrease in the acidity of the catalyst.

To understand the role of indigenous or added inorganic compounds in CFP of biomass, and the potential ash/catalyst interactions that may take place in CFP, the influence of them on the distribution and composition of products resulting from the primary and secondary fast pyrolysis reactions has to be examined. Parameters such as the type and the condition of the catalyst, and the presence of inorganic constituents in the biomass, could be used to alter the relative rates of the biomass decomposition and subsequent vapour phase reactions, and eventually produce pyrolysis liquids with an improved composition. Fig. 1 shows the possible effects of the presence of the ash (whether or not accumulated during the process) on the activity of the catalyst in catalytic fast pyrolysis of biomass. Hypothetically, four different pathways can be distinguished on how the ash influences the vapour phase chemistry and the activity of the catalyst. It should be noticed that combined effects are possible too.

1. The catalytic effect of ash itself on the primary pyrolysis vapours results in the increased production of non-condensable gases (NCGs) and char.
2. Ash may crack some larger vapour phase molecules inaccessible to the catalyst's interior, to smaller ones which are capable of entering the catalyst pores.
3. Cracked vapours may then either be further reformed by the catalyst (a) or not (b).
4. Ash particles poison the catalyst and (negatively) affect the vapour conversion and the reaction chemistry.

The objective of this paper is to investigate the effects of indigenous and/or added biomass ash and its major constituents on the