

Valorization of hazardous organic solid wastes towards fuels and chemicals via pyrolysis

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The management of municipal and industrial organic solid wastes has become one of the most crucial environmental problems in modern societies. The objective of this work was to study the application of the pyrolysis method for the conversion of organic hazardous wastes towards high added value fuels and chemicals. The type of wastes considered, comprised of petroleum-based sludges and sediments, residual paints left on used/scrap metal packaging, and treated wood waste that has been impregnated with hazardous substances, i.e. creosote, for conservation purposes. The pyrolysis experiments were carried out on a bench scale, fixed bed reactor at 600 °C, simulating conditions of fast pyrolysis, i.e. fast heating, low vapor contact time and rapid cooling, in order to maximize the liquid product (pyrolysis oil). Prior to pyrolysis, the solid wastes, sludge, treated wood and paint, were dried at 105 °C for 24hrs and were mixed with inert silica sand (mass ratio of ~ 1) which was used to enhance the heat transfer in the pyrolysis bed. Furthermore, with the aim to in situ upgrade the produced pyrolysis oil/vapors, instead of the silica sand, an acidic zeolitic catalyst was used, ZSM-5, which is widely applied in the case of biomass fast pyrolysis for deoxygenating the bio-oil and producing high value aromatic hydrocarbons. Analysis of the pyrolysis oil and gas products was carried out by GC-MS and GC, respectively.

The product yields obtained in the thermal (non catalytic) pyrolysis results are presented in Table 1. The pyrolysis oil obtained from the petroleum oil-containing sludge accounted only for 15.8 wt. % based on mass dry feed, with the gaseous products being also low (7.9 wt.%). On the other hand, the formed char/coke was remarkably high, ca. 75.1 wt.%, indicating enhanced re-polymerization/condensation reactions of the initially formed smaller petroleum fractions/compounds upon pyrolysis at 600°C. Owing to its different nature and composition, the wood waste that had been treated/impregnated with creosote, provided substantially higher oil yield (46.9 wt.%) and lower char/coke (36 wt.%), as well as increased gases (14.8 wt.%). Such product yield distribution is typical for the thermal fast pyrolysis of lignocellulosic biomass, i.e. wood or crops (Iliopoulou *et al.*, 2014). More similar to the treated wood, the oil yield in the thermal pyrolysis of the residual paint from scrap metal was 35 wt.%, and the yields of gases and char/coke were 19.2 and 36.9 wt.%, respectively.

The relative composition of the obtained pyrolysis oils is shown in Figure 1. As expected the petroleum sludge derived pyrolysis oil contained mainly mono-aromatic hydrocarbons, such as p-xylene and 1,3-dimethyl benzene, as well as aliphatics, such as dodecene. The oil obtained from the pyrolysis of the creosote treated wood contained mainly polycyclic aromatic hydrocarbons (PAHs) such as pyrenes and anthracenes most probably derived from creosote, as well as some alkoxy-phenolics originating from the pyrolysis of the wood itself. The paint derived oil contained essentially methacrylate esters, owing to the nature and composition of the paint which was used as marine coating/polish products. The gases that were collected during the thermal pyrolysis of all of the solid waste feedstocks were mostly consisting of CO and CO₂, as well as some C1-C4 hydrocarbons.

Table 1. Product yields and mass balances in thermal fast pyrolysis of various organic solid wastes at 600 °C

Material	Pyrolysis Oil (wt. %)	Gases (wt. %)	Char/coke (wt. %)	Total (wt. %)
Petroleum containing Sludge	15.8	7.9	75.1	98.8
Creosote treated wood	46.9	14.8	36.0	97.7
Residual paint from cans	35.0	19.2	36.9	91.1

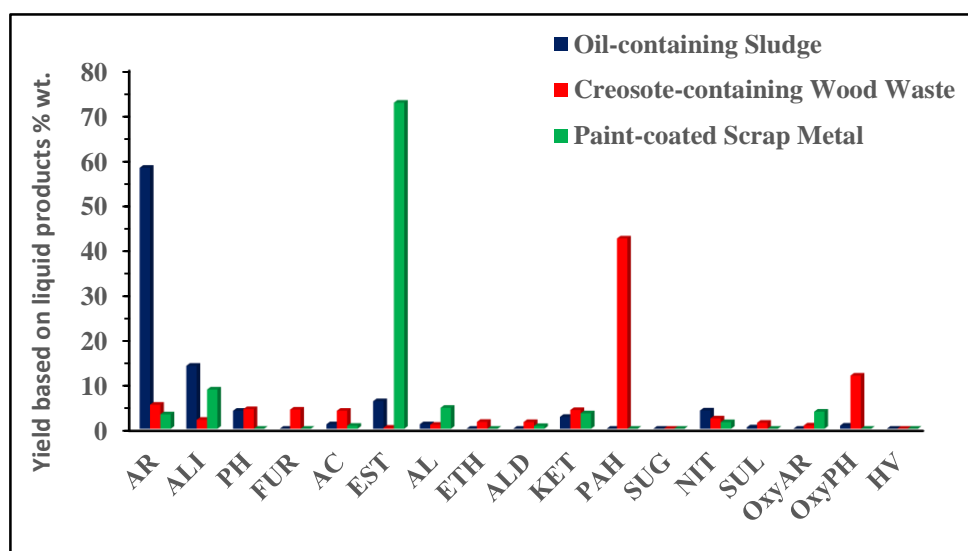


Figure 1. Composition of thermal pyrolysis oils obtained from various organic solid wastes (600 °C)

The results of catalytic fast pyrolysis with ZSM-5, at 600° C, are reported in Table 2. A comparison with the results shown in Table 1 for the thermal (non catalytic pyrolysis) indicates that the use of the acidic microporous ZSM-5 zeolite catalyst shifts the yield towards gaseous products by decreasing both the oil and char/coke. The decrease of char/coke is beneficial and may be attributed to enhanced (due to ZSM-5) cracking of the intermediate oligomers formed upon initial thermal pyrolysis of the organic wastes towards smaller fragments/monomers that condense as liquid product. On the other hand, it seems that the relatively strong acidity and reactivity of ZSM-5, in combination with the high temperature, leads to over-cracking of the oil range compounds towards gaseous products.

The use of the acidic ZSM-5 zeolite affected also the composition of the pyrolysis oils (data not shown), affording increased relative concentration of small, mono-aromatics as well as PAHs with only two benzyl rings (i.e. naphthalenes) compared to the composition of the thermal pyrolysis oils. Due to the over-cracking effect of ZSM-5, the gaseous products contained high concentrations of ethylene and propylene, together with CO and CO₂.

Further optimization studies with regard to tuning of pyrolysis conditions and catalyst's properties are in progress in order to maximize the yield of pyrolysis oils with the desired composition.

Table 2. Product yields in catalytic (ZSM-5) fast pyrolysis of various organic solid wastes at 600° C

Material	Pyrolytic Oil (wt. %)	Gas Products (wt. %)	Char/Coke (wt. %)	Total (%)
Petroleum containing Sludge	16.1	18.3	64.5	98.9
Creosote treated wood	34	28.6	34.3	96.9
Residual paint from cans	27.7	37	26.9	91.6

References

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