Valorization of humin by-products formed during biomass processing *via* gasification / synthesis gas route

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Introduction

Hydoxy-methyl-furfural (HMF) and Levulinic acid (LA) have been identified as top value added building platforms for bio-based fuels and chemicals [1]. Conventionally, these components are produced *via* acid catalyzed dehydration of sugars (e.g., fructose, glucose). The main problem of this catalytic conversion (Figure 1) is the formation of large amounts of solid by-products (yield up to 40%) commonly referred to as humins [1].

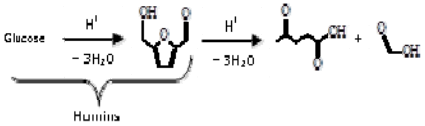

Figure 1. Formation of humin during dehydration of glucose using acid catalyst

Valorization of this recalcitrant waste is essential to make the whole conversion economical. Since they contain high amount of carbon, humins can be used as carbonaceous source for making synthesis gas or hydrogen *via* gasification [2]. In this study, gasification using steam, or carbon dioxide of humin was investigated systematically. Thermal programed oxidation of humin in steam or carbon dioxide showed a weight loss of 45% during heating the sample to gasification temperature (i.e., 700 °C). Therefore, humins undergo transformation prior to reaching gasification temperatures and it is essential to know the morphological and chemical characteristics of the state of humins at gasification temperatures.

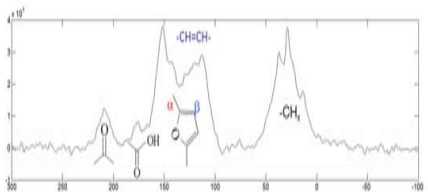

Figure 2 ^{13}C MASNMR of fresh Humin sample

Materials and Methods

Humin formed during six hours of dehydration of glucose using 1M with H_2SO_4 as catalyst at 180 °C was used as model feedstock. The thermal and catalytic (using Na_2CO_3 as catalyst) reforming reaction was performed in thermal gravity experiments in H_2O or CO_2 at atmospheric pressure (concentration 5-40%) and 725-900°C. Samples of humin were characterised by elemental analysis, HR-SEM, Raman Spectroscopy, Solid state C^{13} MAS-NMR. Products formed *via* de-volatilization during heating were investigated using pyro-probe technique and identified using GC-MS.

Results and Discussion

The elemental analysis and solid state NMR results shows that original humin is rich in carbon content (~66%wt C, 4% H and 30% O) and exists mainly in the form of furan ring structure with carboxylic, ketone and aliphatic groups (Figure 2). During heating to gasification temperatures humin undergoes drastic changes in morphology and chemical composition (Figure 3). HR-SEM (Figure 3, inset) shows loss of the bulk and formation of shell type hollow spheres. The [CHO] analyses at various temperature intervals show occurrence of de-oxygenation (Figure 3). During the pyrolytic de-oxygenation, products were monitored by QMS and GCMs and indicated formation water and furanic, (poly)-aromatic products. At the gasification temperature, humin contains mainly aromatic components and resembles graphitic carbon structure.

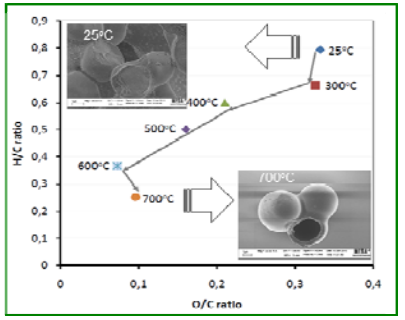

Figure 3 Elemental compositional changes that occur during heating of humin

Thermal gasification (Fig 4) of humin via wet / dry reforming is difficult. Addition of alkali catalysts improves the gasification rate substantially. Almost 100% conversion was achieved at 750 °C in the presence of alkali catalysts for dry reforming. Steam reforming is even more facile and complete conversion can be achieved at still lower temperatures. Among those, sodium carbonate shows highest activity. Catalysis of humin gasification is discussed.

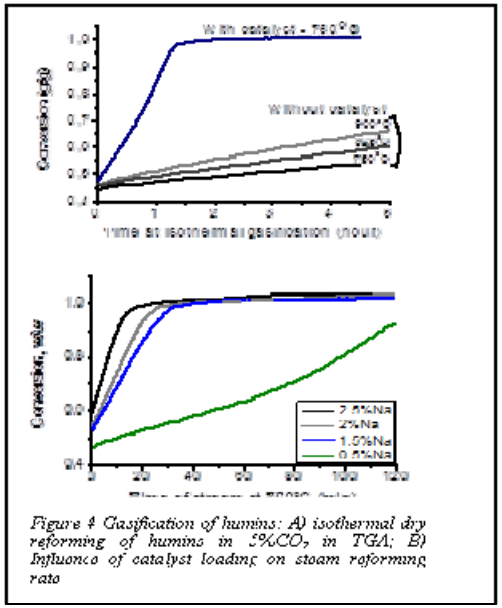

Figure 4 Gasification of humins: A) isothermal dry reforming of humins in 5%CO2 in TGA; B) Influence of catalyst loading on steam reforming rate

References

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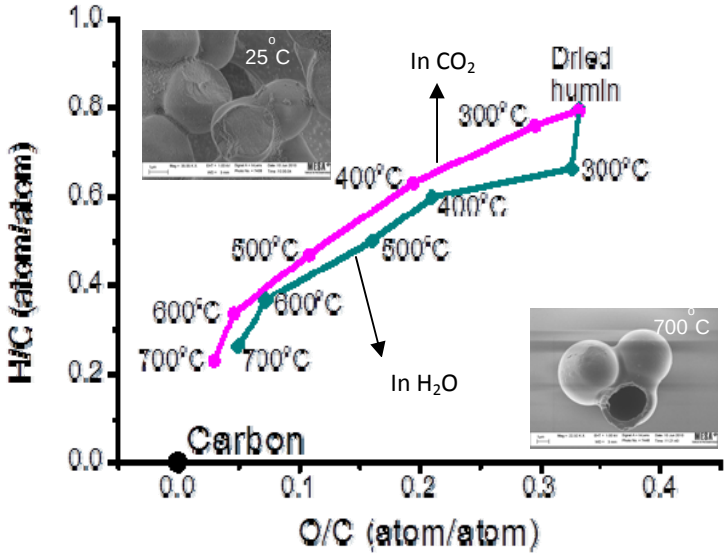
H/C (atom/atom)
O/C (atom/atom)
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.1
0.2
0.3
0.4
25 °C
In CO2
Dried humin
300°C
400°C
300°C
400°C
500°C
500°C
600°C
600°C
700°C
700°C
In H2O
700 °C
Carbon