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

T.M.C. Hoang, L. Lefferts and K. Seshan*
Catalytic Processes and Materials, Faculty of Science and Technology, University of Twente,
P.O. Box 217, 7500 AE, Enschede, The Netherlands
*k.seshan@utwente.nl

Introduction

Hydroxy-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].

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.

Materials and Methods

Humin formed during six hours of dehydration of glucose using 1M with H2SO4 as catalyst at 180 °C was used as model feedstock. The thermal and catalytic (using Na2CO3 as catalyst) reforming reaction was performed in thermal gravity experiments in H2O or CO2 at atmospheric pressure (concentration 5-40%) and 725-900°C. Samples of humin were characterised by elemental analysis, HR-SEM, Raman Spectroscopy, Solid state 13C 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

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.

References
