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Thermal conversion of glucose to aromatic hydrocarbons via pressurized secondary pyrolysis

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ABSTRACT

In this study, glucose, a primary building-block of biomass was subjected to secondary pyrolysis in a reactor that was retrofitted subsequent to a primary micro-pyrolysis reactor. It was observed that incorporation of a secondary reactor resulted in producing significant amounts of gasoline range hydrocarbons. The hydrocarbon yields improved further as a result of increasing pyrolysis reactor pressure and temperatures. The temperature of the secondary reactor was varied between 400 and 800 °C and pressure between 0 and 150 psi. This study indicates that secondary cracking of primary pyrolysis products of biomass oxygenates undergo gas-phase homogenous molecular restructuring. The result of this process is production of substantial amounts of thermodynamically stable gasoline-range hydrocarbons even in the absence of a catalyst.

1. Introduction

Lignocellulosic biomass has been a vital energy source since prehistoric times. Biomass has gained a renewed interest as a starting material to produce transportation fuels. Thermal depolymerization via pyrolysis, liquefaction or gasification is an important intermediate step in processing solid biomass to fuels and chemicals. Unfortunately, a critical drawback of biomass or its derivatives is its high oxygen content which amounts to almost 40% (wt). In any thermal depolymerization process, this oxygen either ends up in product molecules that have fuel value making them energetically less dense, or it gets removed from the process as energetically useless CO_2 or H_2O. Present processes such as hydrodeoxygenation, and Fischer Tropsch (FT) synthesis is geared to catalytically remove oxygen while reforming hydrogen and carbon atoms to produce an array of hydrocarbons that are ultimately refined to use as hydrocarbon fuels.

Thermal conversion processes such as pyrolysis rid the biomass of oxygen and this oxygen leave significantly as CO_2, CO or H_2O. However, during these conversions, a significant amount of oxygen is still retained in as phenols, furfurals, furans, acetic acid and acetaldehyde. Different processes have been developed to make such liquid fraction free from oxygenates. Some of these process are: (a) high pressure liquefaction and aqueous phase reforming of oxygenates (Chheda et al., 2007; Donnis et al., 2009); (b) fast pyrolysis and catalytic treatment of condensable gaseous phase (Adjaye and Bakhshi, 1995a,b, 1994); and (c) catalytic fast pyrolysis (Bridgwater, 1996).

Catalytic fast pyrolysis involves thermal depolymerization of biomass in the absence of oxygen where the vapor-phase pyrolysis products are upgraded via a heterogeneous catalytic process (prior to condensation). According to literature, different catalysts have been tested in this regard (Adjaye and Bakhshi, 1995). For example, zeolytic molecular sieves have shown high substrate conversion and high selectivity toward production of hydrocarbons such as benzene, toluene, ehtylbenzene, and xylene (BTEX) (Gayubo et al., 2004). Although the use of catalysts is desirable for improved kinetics, the rapid rate of deactivation due to coking is an endemic problem (Mohan et al., 2006; Huber et al., 2006). Consequently, these catalysts need to be continuously regenerated burning off coke while at times utilizing hydrogen – which is costly and environmentally malignant. An alternative approach would be to harness the advantages of thermochemistry to optimize BTEX yields and then submit to kinetics to maximize it. In order to find the thermochemical maximum of BTEX yields, the effect of non-catalytic secondary stage pyrolysis reactor on aromatics yield is investigated in this study. Homogeneous reactions that occur in secondary stage pyrolysis is not widely reported and the objective of this study was to fill this knowledge gap. In secondary pyrolysis the uncondensed vapor phase pyrolysis product fraction from the primary pyrolysis is sent through a secondary reactor which is maintained at a specific temperature and pressure. In this secondary stage, the reactor temperature increases the thermal vibrations

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that results in further thermal cracking and molecular rearrangement while the increase in pressure would increase the intermolecular collisions and collisions with the reactor wall.

2. Methods

The reaction was performed using high pressure CDS pyroporbe 5200 micro-reactor that has been retrofitted with a secondary reactor (CDS analytical, Oxford, PA, USA). A glucose sample of ~4 mg (Sigma Aldridge, St. Louis, MO, USA) was placed in a one-inch long micro quartz tube. The sample was secured using quarts wool. The quartz tube with the sample was placed in the probe's filament where the sample was heated at 800 °C. The flow path in the system is shown in (Fig. 1).

The probe's filament was fired for 20 s and the products were passed through the secondary reactor. The secondary reactor was maintained at different temperatures ranging from 400 to 800 °C in 100 °C increments. The products that exit the secondary reactor were purged through a Tenax adsorbent gas trap for 1 min. The reactor pressure was controlled by a backpressure regulator from 0 to 150 psi in 50 psi increments. A steady helium flow rate of 30 mil/min was maintained in the reactor.

Following the adsorption run, the products were desorbed by purging the trap with gas chromatograph's (GC) carrier gas (helium) at 300 °C and routed into the GC inlet. Desorption of the trap and initiation of the GC–mass spectrometer (MS) run was automatically synchronized. The GC–MS analysis was performed using Agilent 7890 GC coupled with Agilent 5890 MS detector (Agilent Technologies, Santa Clara, CA, USA). The column used for the MS analysis was HP-5 ms (30 m, 0.25 mm OD, 0.25 μm ID). The FTIR analysis (Thermo Scientific IS10) of the volatile fraction that did not get adsorbed by the Tenax trap was performed by collecting the gas sample eluting from the trap into a gas cell with KBr windows on both sides. The statistical experiment was conducted as a full factorial design and results were analyzed at $\alpha = 0.05$ significance level using Design-Expert software (Stat-Ease, Inc. Minneapolis, MN, USA).

3. Results and discussions

In this study the pyrolysis temperature was maintained at 800 °C at a heating rate of 1000 °C/s to achieve flash pyrolysis conditions where nearly 90% of glucose would be volatilized. A higher heating rate of 1000 °C/s has to be selected to overcome the high thermal gradient present between the heating filament of the probe and the sample due to the quartz tube wall. It was observed that slow heating rate (<1000 °C/s) of the sample produced significant amount of carbonaceous deposits. It was noticed that during the primary stage pyrolysis large quantities of furfurals were formed. Since Tenax trap does not adsorb light molecular weight hydrocarbons, gas analysis was performed using the FTIR equipped with a gas-cell. This analysis as given in (Fig. 3) indicates a significant presence of CO, CO_2, and CH_4 at different temperatures and atmospheric pressure. According to Fig. 3 the gaseous products significantly increase with increasing temperature. Carbon dioxide yield increases dramatically with temperature implying that in the secondary reactor –C–O– groups were removed as deoxygenated

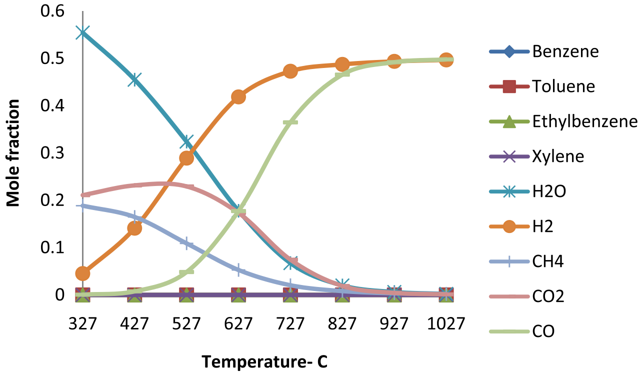

Fig. 2. Thermodynamic equilibrium product composition at 0 psi and at different temperatures.

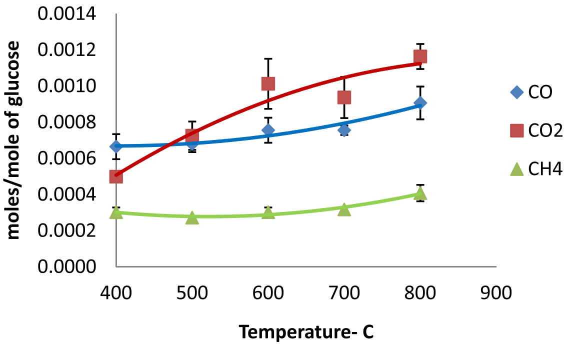

Fig. 3. Gaseous products yield of secondary pyrolysis at 0 psi and different temperatures.

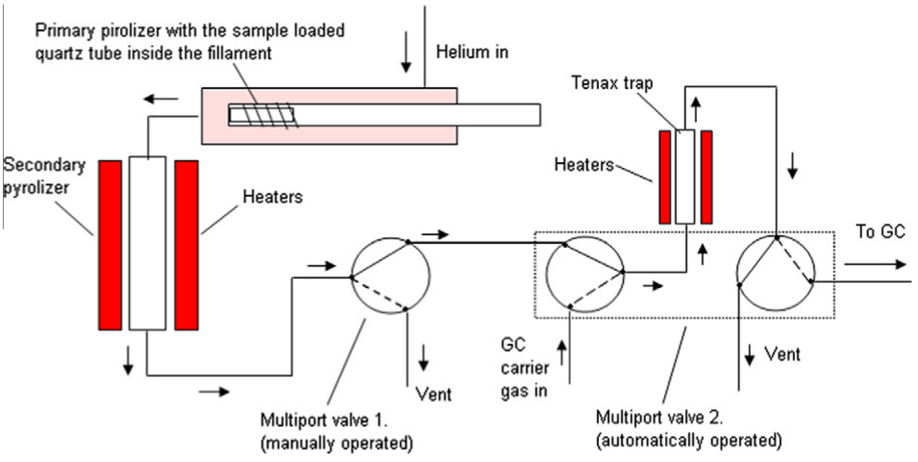

Fig. 1. The line diagram for the combined pyrolizer and the secondary reactor. Multi port valve 1 is manually operated and valve 2 is automatically operated.