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Introduction

Numerous studies have been undertaken to reduce the production of polynuclear aromatic hydrocarbons (PAHs) from the thermal processing of energy resources such as coal and oil.[1] PAHs are also thought to be precursors to soot which are found in the combustion of energy resources.[2,3] In the combustion of coal, volatile organic material is released from the particles primarily by pyrolytic reactions. Once these materials are released, they can undergo additional reactions with the surrounding species to form products, which may then be oxidized in the flame. A better understanding of the initial pyrolysis reactions and subsequent reactions of the vapor phase products could provide considerable knowledge into controlling PAH formation in the thermochemical processing of biomass, reducing soot formation in combustion, and reducing tar formation in gasification.[4]

Because of the complexity of the reaction mixtures from the pyrolysis of biomass and the limited number of fundamental studies on the pyrolysis of biomass model compounds, there is an incomplete understanding of the formation pathways of PAHs from the thermal processing biomass. Therefore, we are currently interested in determining the pyrolysis conditions, reaction mechanisms, and kinetics that lead to PAH formation in the thermochemical conversion of biomass. This investigation will focus on the formation of PAHs from the pyrolysis of plant steroids, because the native cyclic ring structure of the steroid appears to be preorganized to form cyclopentaphenanthrene or phenanthrene by dealkylation and dehydrogenation reactions. Sterols and sterol esters are part of the plant lipid membrane and are found in the nonpolar extract of biomass and in tall oils (from the Kraft process). In Scotch pine foliage, sterol esters (comprised of 84% β-sitosterol, stigmasterol, and campesterol) constituted 1.1 wt% of the dry foliage.[5] In pine tall oil, the major nonsaponifiable compounds were steroids and diterpenes.[6]

Many of the kinetic and mechanistic investigations of plant steroids have been performed at relatively low temperatures (<500 ^{0}C) and long residence times (>1 min), since steroids are used as biological markers to indicate the maturity of sediments. Badger et al. investigated the flow pyrolysis of stigmasterol at 700 ^{0}C (unknown residence time) over porcelain chips and significant quantities of benzene (11.7 wt% of tar), naphthalene (12.3 wt%), phenantherene (12.1 wt%), and chrysene (13.2 wt%) were found.[7] It was concluded that the PAHs could be formed by dehydrogenation reactions rather than by pyrosynthesis (i.e., initial cracking into small fragments, such as ethylene, acetylene, and butadiene, followed by radical addition and cyclizations reactions).[8] The same mechanisms (i.e., radical addition reactions of C_2-C_5 hydrocarbons to aromatic rings) have been postulated for PAH formation and growth in fuel-rich flames.[9,10] Severson et al investigated the pyrolysis of an equal mixture of stigmasterol, β-sitosterol, and cholesterol at 700 ^{0}C under conditions in which the PAH ratios from the pyrolysis of tobacco were similar to the PAH profiles found in cigarette smoke condensate.[11] The major aromatic products were phenanthrene, methylated phenanthrenes/anthracenes, chrysene, and methylated chrysenes/1,2-benzanthracenes. Minor amounts of benzo[a]pyrene and benzo[e]pyrene were also found. The high yields of phenanthrene in these studies suggest that the steroid ring dehydrogenates to form phenanthrene and undergoes additional reaction to form chrysene.

In the investigation, the pyrolysis of stigmasterol was investigated since this steroid, shown in **Figure 1**, is typically found in plant foliage. The pyrolysis was investigated from 600-800 ^{0}C at residence times of 0.135-1.0 seconds to determine the effect short residence times on the yield of PAH formation, which are relevant to conditions found in fuel processing. The effect of concentration on PAH yields will also be investigated.

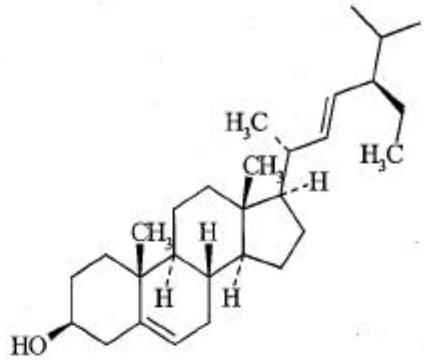

Figure 1. The structure of stigmasterol.

Experimental

Carbon disulfide (Acros 99.99%), hexane (B&J or EM HPLC grade), stigmasterol (Acros, 93.6% by GC), stigmasterol acetate (Sigma, 93.5% by GC) were used without further purification. Phenethyl Acetate (Acros) was purified by vacuum fractional distillation before use (purity 99.0% by GC with phenethyl alcohol as the largest impurity 0.6%). Hexatriacontane and PAH standards (for authentic retention times) were obtained from Accustands and perdeuterated PAHs (phenanthrene-d_{10}, 1,2-benzanthracene-d_{12}, benzo[a]pyrene-d_{12}) were obtained from Aldrich Chemical Company.

In a typical run, a pyrolysis tube was placed inside the horizontally mounted three-zone Carbolite tube furnace 17.7 long and allowed to equilibrate with helium for 20 minutes. The pyrolysis tube is made of three different sizes of quartz fused together: a 12 in. by 3/4 inch o.d. quartz tube (sublimation chamber) connected to a 19 in. by 2.1 mm i.d. quartz tube (the reaction chamber) which tapers to 1/4 in. o.d. piece of tubing 2 in. long (exit to the first trap). A mass flow controller (MKS Instruments) was used to control the helium flow through the pyrolysis tube. A quartz boat (1 in. x 5/8 in. x 3/8 in.) was charged with a known amount of substrate (typically 200 mg) and placed in the pyrolysis tube about 4.5 inches from the entrance of the furnace. The sample reaction chamber was heated via an aluminum shroud wrapped with heat tape, and the temperature was monitored via a thermocouple in the aluminum block and one next to the sample. The concentration of the substrate was determined by the sublimation rate, which is controlled by the temperature of the aluminum shroud, and the gas flow rate. The residence time for the sample in the furnace was calculated from the volume of the reactor in the hot zone (1.06 mL), and the gas flow rate at room temperature. A correction was applied for the volume expansion of the gas from room temperature to the reaction temperature at atmospheric pressure. Two exit traps were used and connected in series via 1/4 inch ball joints and attached to the exit portion of the pyrolysis tube. The first trap, which is made of glass, is 11 in. by 3/4 in. o.d. and tapers to a 1/2 in. i.d. piece of tubing 9 in. long. Carbon disulfide (3 mL) was added to the first trap for solubility of the pyrolysized sample, and the trap is cooled in a dry ice/acetone bath. The second glass trap, 8 in. by 1/2 in. o.d., contains a 2 in. by 1/2 in. entrance arm 3 in. from the top with a ball joint connector fitted on the end. The trap is placed inside a 6 in. by 3/4 in. glass tube, cooled to 77K (liquid N_2), and the tip of the exit tube is 1 in. deep into a loosely packed plug of clean glass wool. The glass wool traps aerosol particles formed at high flow rates (>100 mL min^{-1}). A digital gas flow meter (Alltech) is attached to the second exit trap to monitor the gas flow through the pyrolysis tube. The flow pyrolysis experiment was complete when the substrate does not condensate within the inside diameter of the first exit trap after the allotted time. After the pyrolysis, the reaction chamber temperature

is reduced to allow the sample boat to cool to room temperature, while the flow rate is decreased (typically 3-5 mL min^{-1}). Both traps and the glass wool were extensively washed with carbon disulfide (total volume 15-20 mL). Solutions of hexatriacontane, phenanthrene-d_{10}, 1,2-benzanthracene-d_{12}, benzo[a]pyrene-d_{12} were added as standards, and the samples were analyzed and quantitated by GC and GC-MS.

Product identification was determined by comparison of GC retention times and mass spectral fragmentation patterns from authentic samples and from the NIST mass spectral library. Products were quantitated by GC with flame ionization detection (FID) and internal standards. All samples were shot on the GC at least three times by a HP 7673 autosampler, and the data was averaged. Typical shot to shot reproducibility was ±2%, but larger errors (±10%) were found in quantitating some of the smaller products (<0.1 mol%) in the presence of a large background. Response factors were measured, estimated from measured response factors for structurally related compounds, or estimated on the basis of carbon number. Reaction mixtures were analyzed on a Hewlett Packard 5890 Series II Plus gas chromatograph employing a J&W DB-5, 5% diphenyl-95% dimethylpolysiloxane capillary column (30 m x 0.25 mm id. with 0.25 μm film thickness). The injector temperature was at 280 ^{0}C, and the detector was 305 ^{0}C, respectively. The carrier gas was helium at a constant flow rate of 1 mL min^{-1}. The oven program was started at 45 ^{0}C, held for 1 min, ramped at 10 ^{0}C min^{-1} to 300 ^{0}C, and held for 15 min. Mass spectra were obtained at 70 eV with a Hewlett Packard 5971A/5972 mass selective detector and a capillary column identical to that used for GC-FID analysis. The authentic GC detector response factors for the 3, 4, and 5-ringed PAHs were determined relative to perdeuterated phenanthrene, benzanthracene, and benzo[a]pyrene, respectively, as internal standards. All other products were quantititated relative to hexatriacontane. Before the flow pyrolysis of stigmasterol was investigated, the reactor was calibrated by the pyrolysis of phenethyl acetate, whose well-defined first order kinetics allows verification of the reactor temperature and residence time.[12] It was found that the flow reactor reproduced the literature parameters for the kinetics of pyrolysis of phenethyl acetate at 500-600 ^{0}C and residence times 0.135-1 s.

Results and Discussion

The flow pyrolysis of stigmasterol was studied as a function of temperature at 600, 700, and 800 ^{0}C at short residence times (0.135 s) and long residence times (1.0 s). **Figure 2** shows selected aromatic products produced from the flow pyrolysis of stigmasterol. These products range from the low molecular species (such as benzene, toluene, styrene) to the larger scale molecular weight PAHs (naphthalene, phenanthrene, chrysene) and their yields will vary depending upon the reaction temperature and residence time. In this paper, we will only focus on the 3, 4, 5-ringed PAHs formed.

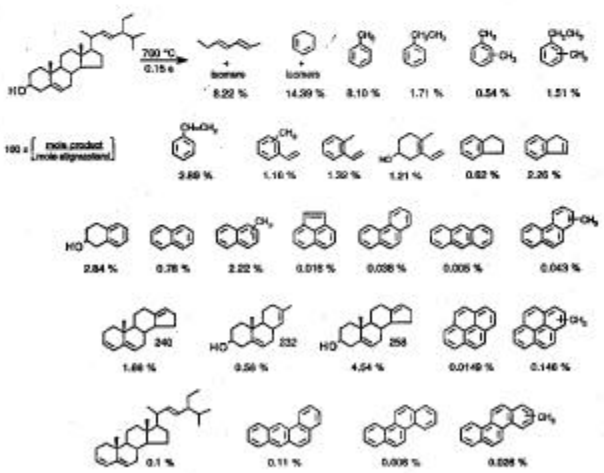

Figure 2. Selected aromatic products produced from the flow pyrolysis of stigmasterol.

Stigmasterol was sublimed under a flow of helium at a rate of 0.90 mg min^{-1} (low concentration) and 77 mg min^{-1} (high concentration) so that the gas phase concentrations were between $1x10^{-3}$–$1x10^{-6}$ M. All reactions were run in duplicate to determine the reproducibility (± 15% variation of the product yields (mg/g) between runs). Based on recovered starting material at the short and longer residence times, the conversion increased from 85.4%, 99.8%, to 100% as the temperature increased from 600, 700, and 800 ^{0}C, while the mass balance decreased with temperature. The low mass balances determined in the flow pyrolysis arise from quantitation of only the major products (which account for ca. 55% of the GC area), and from the formation of the light gases that are not quantitated. Propene, butene, butadiene, pentene, and pentadiene were observed in GC-MS analysis of the reaction mixtures, but were not quantitated because of their volatility. At 650 ^{0}C, the pyrolysis under low concentration (0.90 mg min^{-1}) was investigated as a function of residence time (0.135 – 2.0 s), and the yields of selected PAHs are shown in **Figure 3**. As the residence time significantly increased the yields of small and large PAHs. As the residence time increased, the yield of many of the products, such as phenanthrene and anthracene, increased linearly with residence time.

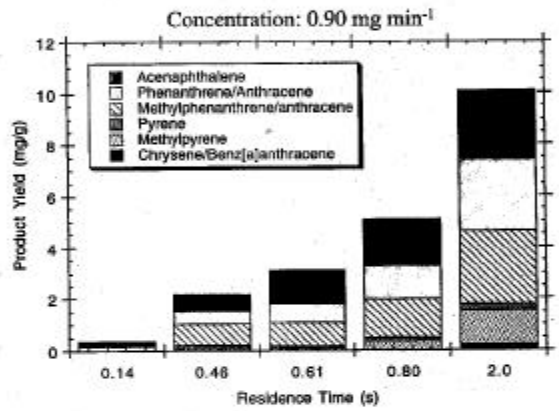

Figure 3. Effect of residence time on PAH formation from the pyrolysis of stigmasterol.

The effect of concentration on PAH yields is shown in **Figure 4** between the low concentration (0.90 mg min^{-1}) and high concentration (77 mg min^{-1}) pyrolysis experiments at a shorter residence time of 0.135 s. Surprisingly, the total yield of three- to five-ringed PAHs only increased a factor of two for a 75-fold increase in concentration. However, the yield of four- and five-ringed PAHs (chrysene, benz[a]anthracene, pyrene, and benzo[a]pyrene) increase more dramatically (3-5 fold) at high concentrations.

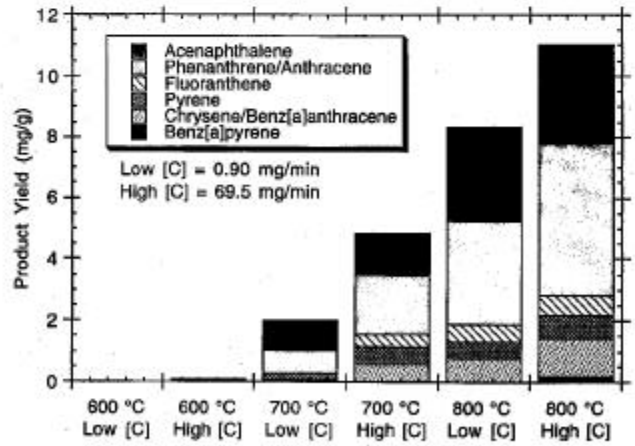

Figure 4. Comparison of High and Low Concentration PAH Yield Formation.

To determine the impact of temperature on the yields of PAHs at high concentration (77 mg min^{-1}), the substrate was sublimed at 460 ^{0}C. In **Figure 5**, at 600 ^{0}C short residence time (.135 s), over 85% of the stigmasterol was consumed and no PAHs larger than fluorene was produced. Small quantities of PAHs with three rings or more were only found at 600 ^{0}C longer residence time (1.0 s) (>99.8% conversion of the stigmasterol). At 700 ^{0}C (0.135 and 1 s), there was a 30% increase in the yields for the two, three, and four ringed PAHs produced in comparison with the data at 600 ^{0}C. Experiments at 800 ^{0}C (0.135 and 1 s) showed a 50% increase (comparison with the data at 700 ^{0}C) for the yields of aromatics (benzene, phenanthrene, and anthracene), however the yields of dihydroaromatics (1,3-cyclohexadiene, indan, and 1,2-dihydronaphthalene) decreased. At higher temperatures, dehydrogenation reactions to form PAHs become more favorable. Studies investigated by Britt et al help support the assumption that the native cyclic ring structure of the steroid is preorganized to form phenanthrene based PAHs, by dealkylation and dehydrogenation reactions.[13] This comparison highlights the importance of residence time on the yield of PAHs. A 7-fold increase in residence time increased PAH yields 3-6 fold at 600, 700, and 800 ^{0}C respectively. It was also discovered that similar yields of PAHs could be obtained at low temperatures and long residence time or at high temperatures (i.e., 800 ^{0}C) and short residence times.

Conclusions

The investigation into the pyrolysis of stigmasterol showed that residence time affects PAH yields more than concentration (over the limited range of concentrations and residence times evaluated). Clearly, PAH formation is enhanced at longer residence times and higher temperatures. At short residence times (0.135 s), smaller amounts (<3 mg/g) of PAHs, such as phenanthrene, anthracene, flouranthene, chrysene, benz[a]anthracene, and methylated PAHs were found compared to longer residence time (1.0 s). Increasing the concentration 75-fold increased the total yield of 3- and 5-ringed PAHs only by a factor of two, but the yield of 4- and 5-ringed PAHs (chrysene, benz[a]anthracene, pyrene, and benzo[a]pyrene) increase more dramatically (3-5 fold) at high concentrations. Also, temperature was shown to have a significant impact on the PAH yields with yields significantly increasing at temperatures >700 ^{0}C.

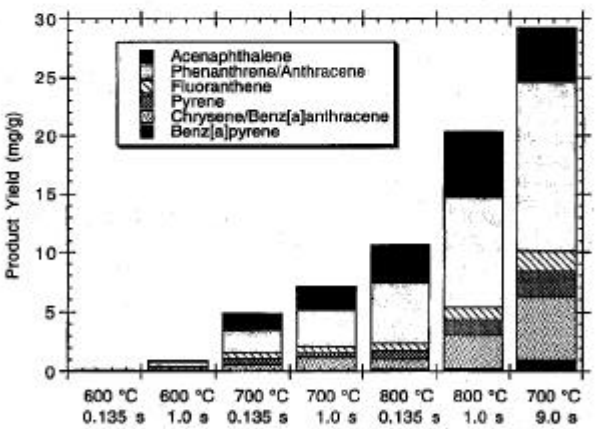

Figure 5. Effect of High Concentration of PAH Yield.

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