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Analysis of tars formed during co-pyrolysis of coal and biomass at high temperature in carbon dioxide atmosphere

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ABSTRACT

The analysis of tars from the high temperature (1573 K–1773 K) co-pyrolysis of coal (Pittsburgh #8) and biomass (Switchgrass and White Pine) in CO₂ has been carried out.

The analysis shows that naphthalene content is the maximum in all the tar samples irrespective of biomass and coal blend proportion. Samples with high percentages of coal as well as experiments conducted at 1773 K showed the highest concentration of aromatic compounds. The largest aromatic compound found had five benzene rings (benzo(e)pyrene). Aliphatic hydrocarbons as well as oxygenated hydrocarbons were mostly found in samples containing high percentages of biomass or in experiments conducted at 1573 K. About 100 compounds have been identified in the tars of which 25% account for 90% of the mass of tar.

The study indicates that the atomic N/C and S/C ratio increases whereas H/C ratio decreases with pyrolysis temperature. The rate of variation of H/C ratio reduces as the temperature increases. The biomass content in the fuel feed seems to have an impact on the H/C ratio of the tars only at lower temperatures. That is, at lower temperatures, the higher the biomass content of the fuel, the higher the H/C ratio of the resulting tars. These observations also apply to the O/C ratio of the tar. For both switchgrass and pine sawdust, the biomass content of the fuel seems to have no influence on the nitrogen content of the tars. The distribution of sulfur in the tar is inversely proportional to the biomass percentage in the fuel. The higher the biomass content of the fuel, the lower the atomic S/C of the tars.

1. Introduction

Tars are a group of compounds obtained during the rapid devolatilization of coal or biomass that can condense and cause depositional problems and therefore merit special investigation, especially when biomass and coal are blended. There is no universal definition for tars in the scientific community. Tars are a collection of several compounds, and their quality and quantity vary from one operating condition to another. Therefore, the terms “tars” and “tar” will be used interchangeably in this text. Nevertheless, a commonly used definition of tars is that they are a class of volatile species in the gas phase that become condensable below a certain temperature in the reactor or in downstream processes and conversion devices. Although this definition covers a wide range of compounds, the species that form tar are mostly aromatic [1]. According to the International Energy Agency (IEA) Gasification Task, any organics that boil at a temperature above that of benzene should be considered as tar.

Although not completely understood, it is accepted that tar

formation during thermal conversion of coal takes place through the following steps [2]:

- i) Depolymerization by rupture of weaker bridges in the coal macromolecule to release smaller fragments that make up the “metaplast.”
- ii) Polymerization (cross-linking) of metaplast molecules and transport of lighter molecules away from the surface of the coal particles by combined vaporization and gas phase diffusion.
- iii) Internal transport of lighter molecules to the surface of the coal particles by convection and diffusion in the pores of non-softening coals and liquid-phase or bubble transport in softening coals.

The formation and speciation of components forming tar is highly dependent on the severity (heating rate, temperature, pressure and residence time) of the thermal conversion process. Secondary pyrolysis reactions involving tar and occurring in the gas phase generate light gases and soot. These reactions are influenced by many factors such as

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the type of coal or biomass, heating rate, residence time, temperature, intra- and extra-particle heat transfer and physical properties of the reacting fuel, such as porosity and swelling and softening properties [3].

According to Evans and Milne [4,5], biomass pyrolysis products from various reactors can be classified as primary (Class I), secondary (Class II) and tertiary (Class III and IV). Using a molecular beam mass spectrometry (MBMS), these researchers' distinguished four classes of products resulting from gas-phase thermal cracking reactions.

The effects of temperature on pyrolysis/gasification with regard to product distribution can be segregated into two temperature regimes: lower temperatures and higher temperatures. Low-temperature pyrolysis results in a gradual decrease of tar as the operating temperature increases, and the maximum pyrolysis temperature here is around 973 K [6–9]. In this temperature range, the heating rate does not appear to have a great impact on the product distribution, especially the amount of tar [10]. At higher temperatures (above 973 K), the amount of tar decreases at a rate higher than that at lower temperatures [11–15].

Detailed characterization of tars can provide meaningful information. It can help predict the amount and constituents of tars in processes in which liquid product yield needs to be maximized or minimized. For instance, minimizing liquid product yield is required in coal or biomass gasification since tar in the product gas is undesirable. However, in combustion processes, tar becomes a valuable product, as it carries a significant amount of the fuel's volatiles. In pyrolysis processes, tar is even more highly valued, as many species that form tar are the main constituents of bio-oil. Quantification and characterization of tar can also provide useful insight into the mechanism of thermal breakdown of solid fuels. Tar forms a significant part of volatile products, accounting for up to 40% of the dried ash-free (DAF) weight of some bituminous coals. Particle size and reactor conditions also have a substantial influence on tar yield. In combustion and gasification, tar plays an important role in controlling flame stability since the low temperature tar product, which is the highest of the initial yield of volatiles gets ignited earlier than other volatiles. It is also the main precursor of soot and thus is relevant to radiative heat transfer, especially when that radiative heat transfer is the dominant mode of heat transfer in entrained flow gasification. The tar formation process has a strong linkage to the char plastic phase as well as char's subsequent physical and chemical structure during the thermal conversion of coal, which therefore influences the swelling and reactivity of the char. The release of primary tars provides meaningful insights into the structure of the parent coal since tar molecules are usually minimally disturbed coal molecular fragments. In gasification systems, tar in the product gas can become detrimental since it causes fouling, coke deposit and catalyst deactivation. A comprehensive characterization of the tars produced from various feedstocks and operating conditions is essential for controlling its enhancement or destruction. Such detailed information (chemical composition, molecular weight, heating value, etc.) needed when conducting modeling studies are critically scarce, especially for high temperature and co-firing operations.

Experimental studies investigating the formation and characterization of tars at high temperatures are not very common. Besides, studies involving co-pyrolysis or co-gasification of coal and biomass at the high temperature range are rare. Song et al. [16] investigated the structure and thermal properties of tar from gasification of agricultural crop residues. However, they used a fixed bed downdraft gasifier operating at a maximum temperature of 873 K to generate the tar. So their studies is only applicable to low/medium temperature biomass tars. Zhu et al. [17] quantified tar yields during co-pyrolysis of Chinese Yinning coal (bituminous) and Poplar sawdust and found that blending coal and Poplar sawdust had an inhibiting effect on tar yields during pyrolysis. However, their experiments were conducted in a Thermogravimetric Analyzer (TGA) with slow heating rate of 10 K/min and operating temperature of 1273 K and an aluminum retort operating at 783 K with

a heating rate of 5 k/min. These operating conditions are not close to commercial entrained flow gasifiers which exhibit high heating rates and high operating temperature (~1673 K). Tag et al. [18] found that the yield and quality of the tar improved during the co-pyrolysis of Shenmu coal and cotton stalk in a quartz tubular reactor with fix bed operation. Again, not only the operating temperature was low (873 K), the heating rate was very slow (5 K/min). Dufour et al. [19] used a tubular reactor operating between 973 and 1273 K to derive a linear relationship between benzene and methane yield as well as total tars and ethylene yield during wood chip pyrolysis. However, this study once again was conducted on a single fuel, at medium temperature and did not provide a conclusive characterization of tar species found. One of the rare studies that investigated tar in an entrained flow reactor is that of Storm et al. [20] who co-pyrolyzed a German high volatile hard coal with biomass and sewage sludge at temperature as high as 1473 K. Although quantitative measurements of tars were done in this study, no characterization work was performed.

In a nutshell, most of the studies investigating the formation and composition of tars in biomass and coal thermochemical processes [21–30] have been conducted at conditions not similar to the operating condition of entrained flow gasifiers. These studies have been conducted mostly in fluidized and fixed-bed reactors offering a maximum temperature of approximately 1473 K. Therefore, studies focusing on the formation and characterization of tar in high-temperature systems such as entrained flow reactors are scarce. One possible reason for this is the belief that tars are completely destroyed at higher temperatures. The present study aims to bridge the gap that exists in the characterization of tars formed during high-temperature pyrolysis of coal and biomass.

2. Materials and method

2.1. The pyrolysis unit

A high-temperature Entrained Flow Reactor (EFR) was used to convert coal, biomass and coal/biomass blends into gases, char and tars. Details of the entrained flow reactor can be found in a previous publication [31]. Pittsburgh #8 Bituminous coal, White Pine sawdust and Switchgrass powder have been used as fuels for these experiments. The blends of coal and biomass fuels are presented in Table 1:

Experiments have been conducted at three temperatures: 1573 K, 1673 K and 1773 K. The flow rate of the primary gas (transport gas) has been maintained at 10 g/min at standard temperature and pressure (STP) while that of the secondary gas has been maintained at 30 g/min at STP throughout the experiment. CO₂ has been used as the primary as well as the secondary gas. A screw feeder has been used to accurately feed the coal and biomass samples at the rates of 1.3 g/min and 1.0 g/min, respectively. Tables 2 and 3 show the proximate and ultimate analyses of the coal and biomass used in these experiments, respectively.

2.2. Tar collection during pyrolysis experiments

A tar sampling train as shown in Fig. 1 has been designed to capture all condensable volatiles and moisture leaving the reactor in the gas

Table 1
Blend ratios of coal and biomass fuels used in the experiments.

Biomass%	Pine sawdust (SD)	Switchgrass Powder (SG)
100	100% SD	100% SG
75	75% SD 25% Coal	75% SG 25% Coal
50	50% SD 50% Coal	50% SG 50% Coal
25	25% SD 75% Coal	25% SG 75% Coal
100	100% Coal	100% Coal

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