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Thermogravimetric heat and mass transfer: Modeling of bitumen pyrolysis

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HIGHLIGHTS

- Bitumen fumes form explosive mixtures with air above about 300 °C.
- According to TGA experiments, bitumen pyrolyses in stages at 250, 350 and 450 °C.
- Three lumped reaction rates characterize the mass loss of bitumen with temperature.
- Increasing the temperature ramp shifts the TGA curves towards the right.
- Below 350 °C, the composition of the condensed vapors is constant.

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ABSTRACT

Mobile reservoirs heat bitumen to temperature exceeding 240 °C thereby reducing the viscosity to pump and make it easier to spread to seal roof tops. Aerosols, vapors and gases evolve at this temperature but more fumes are generated at the surface of the burner where it exceeds 300 °C; these fumes represent a safety hazard. The Cleveland open cup flash point was 320 °C and the Pensky–Martens closed cup flash point was 310 °C for the bitumen tested. Based on thermo-gravimetric analysis, bitumen pyrolysis occurs in three stages. A first fraction (35%) evolves at 250 °C, a second fraction (65%) releases at 350 °C and finally a third fraction (5%) at 400 °C, with activation energies of 52 kJ mol^{-1}, 132 kJ mol^{-1} and 228 kJ mol^{-1}, respectively. Increasing the heating rate shifts the thermo-gravimetric curve towards higher temperature and raises the maximum decomposition rate. We attribute the shift in the curve to heat and mass transfer resistance between the bitumen surface and the inert gas flow. The heat transfer coefficient between the gas phase and the liquid in the crucible varies from 10 W m^{-2} K^{-1} to 20 W m^{-2} K^{-1}, which was estimated by evaporating a solution of glycerine and isobutanol. These ideal compounds were chosen to derive the heat and mass transfer rates, which we applied to the bitumen experimental data.

1. Introduction

Bitumen is a black, viscous and complex mixture mostly composed of hydrocarbons and a small quantity of structurally analogous heterocyclic compounds. Its chemical composition is described according to its proportion of saturates, aromatics, resins and asphaltenes (SARA fractions) [1]. Because of its binding and waterproofing characteristics, bitumen is primarily used in road construction and roofing applications. The Mesopotamians waterproofed their tanks and temple baths with asphalt.

Bitumen is a visco-elastic fluid with a high viscosity below 70 °C, which makes it an ideal binder for asphalt. Above 140 °C its viscosity is low enough to pump. Lesseur et al. published an exhaustive study on bitumen composition, properties and rheological characteristics [2]. They adopted a colloidal model in which the solid particles (the asphaltenes) are dispersed in an oily liquid matrix (the maltenes) at the nanometric level. Michalica et al. studied the relationship between chemical and rheological properties. They concluded that the molecular weight and especially the polarity of the bitumen compounds play an important role in determining the bitumen's physical behavior [3].

In roofing applications, the effluent of a propane burner circulates in coils immersed in the bitumen. Locally, the temperature around the coils exceeds the flash point of >260 °C (Eurobitume, 2011) [4,5]. The temperature of the coils may cause thermo-oxidative decomposition, which represents a safety hazard, in particular when reservoirs are open to atmosphere.

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Kök et al. studied the oxidative decomposition of crude oil in a limestone matrix and identified three distinct reaction steps: low-temperature oxidation (LTO), fuel deposition (FD) and high-temperature oxidation (HTO) [6,7]. Murugan et al. report a two-stage thermal decomposition for the pyrolysis of Athabasca bitumen [8]. They also found considerable differences in the activation energy corresponding to each stage. Park et al. pyrolyzed Alberta oil sand and reported similar results [9]. According to Benbouzid et al., bitumen with a 40/50 and 20/30 penetration grade, decompose in one and two stages, respectively [10]. Also Jing-Song et al. agree on a two-stage mechanism to describe bitumen pyrolysis [11]. Sonibare et al. studied the thermo-oxidative decomposition of Nigerian oil sands bitumen in air [12]. They propose a three-stage decomposition mechanism: LTO, FD and HTO. Hassan et al. report that the activation energy decreases when the oxygen concentration increases [13].

Ollero et al. [14], Gomez-Barea et al. [15] and Jess et al. [16] derived the kinetics of gasification by TGA and included diffusional mass transfer. Ebrahimpur et al. studied the diffusional effects of the oxidation of SiC powders by TGA) [17]. Surov ([18] and Price [19] concentrate on the application of thermogravimetric techniques for determining the saturated vapor pressure of pure organic compounds.

Also, non-thermo gravimetric analyses were used to study the kinetics of the thermo-oxidative decomposition of heavy oils and bitumen. These techniques are useful to evaluate the potential of in situ combustion and thermal recovery process to produce oil. Effluent gas analysis techniques are also useful to derive the reaction kinetics. Moore et al. designed a vessel to study the oxidation behavior of Athabasca oil sand bitumen where the temperature was ramped sequentially along the length to simulate a adiabatic flame front [20]. Belgrave et al. studied on the kinetics of aquathermolisis of bitumen and Albertan heavy oils deposits and derive a kinetic model considering the individual first-order reactions of coke and asphaltenes (ASPH), heavy oil (HO), light oil (LO) and gas components [21]. Corbetta et al. and Ranzi et al. propose a multi-scale approach to model complex kinetics and multi-phase reactors with multi-components [22,23].

Roofing applications have particular safety risks. An operator of a mobile unit was killed when a mixture of bitumen vapors and air exploded while he was on the top of the reservoir [24]. When the mobile reservoir heats up, longer chain molecules thermally decompose and volatile compounds evaporate and fill the vapor space above the bitumen. These vapors can form an explosive mixture when air leaks into the reservoir.

Here, we evaluated the apparent kinetics of bitumen thermal decomposition (and evaporation) by TGA and attribute the change in mass loss to heat and mass transfer resistance. The mass change in the TGA depends on heating rate, which indicates that heat and mass transfer may be rate limiting steps. To assess the mass transfer phenomena, coincidentally with the bitumen TGA tests, we measured the change of mass with time of a glycerine–isobutanol bi-component mixture. The differential curves clearly show three distinct phases, so we have adopted a three lumped parameter model.

2. Experimental

2.1. Materials

Bitumar Montreal manufactured the roofing bitumen used in this work in compliance with ASTM-D312 [25]. Its softening point varied from 57 °C to 107 °C, its penetration from 12 to 60 (100 g/5 s/0.1 mm). The density was 962 kg m^{-3} at 160 °C and 936 kg m^{-3} at 220 °C. The viscosity was 16.2 Pa s at 140 °C and 1.19 Pa s at 180 °C.

To model the bitumen TGA curves we tested a bi-component mixture consisting of a 50% mass fraction of glycerine and 50% isobutanol (>99.5%, Sigma Aldrich). The density of the glycerine is 1250 kg m^{-3}. The boiling points of glycerine and isobutanol are 286 °C and 108 °C at 1 bar, respectively.

2.2. Thermogravimetric analysis

A TA-Q5000 thermogravimetric analyzer recorded the TG curves of 5 mg and 20 mg bitumen samples heated from 20 °C to 600 °C at a rate of 5 K min^{-1}, 10 K min^{-1}, 20 K min^{-1} and 30 K min^{-1} under 75 ml min^{-1} nitrogen. The liquid samples were loaded to a 100 μl platinum crucible. A Platinel II thermocouple placed 2 mm above the sample pan measured the temperature. The balance mechanism has a resolution of 0.1 μg and accuracy better than ±0.1%. The mass change with temperature at 1 K min^{-1} was very close to the test at 5 K min^{-1}. Although temperature ramps greater than 10 K min^{-1} are non-standard, we chose the higher ramp temperatures to accentuate heat and mass transfer effects. For the glycerine–isobutanol mixture, we loaded 5 mg and 20 mg to the crucible and heated the system at a rate of 5 K min^{-1} and 20 K min^{-1} (Table 1). Experiments were repeated three times and reproducibility was excellent.

2.3. Flash point

We measured bitumen's flash point temperature according to the Cleveland open cup test and the Pensky–Martens closed cup test.

2.3.1. Cleveland open cup test

The equipment consisted of a 100 mL cup, heating plate and a propane flame (ignition source). A hot plate heated a 70 mL sample of bitumen at a rate of 5 K min^{-1}. When the temperature reached 230 °C (30 °C below the expected flash point) the propane flame was directed at the cup while maintaining the same temperature ramp. We assigned the flash temperature when we first saw the vapors flash.

2.3.2. Pensky–Martens closed cup test

The test apparatus consisted of a 100 mL cup, cover and shutter, heat plate with stirrer, a propane flame, and a thermometer. A hot plate heated a 70 ml sample of bitumen at a rate of 5 °C min^{-1} while stirring. Starting from 30 °C below the expected flash point (260 °C), we directed a propane flame to the test cup at 10 s intervals, until we detected a flash. The experimental procedures and dimensions of the equipment are described in ASTM-D92-11 [26] and ASTM-D93-11 [27].

2.4. Bitumen vapors

To characterize the compounds that evolve during heating, we placed 30 g of bitumen in a 500 mL flask immersed in a sand bath on a hot plate. Air entered the flask and then passed through a water quench maintained at 0 °C to capture the condensable fraction of the gas and the non-condensables were collected in a second vessel from which we withdrew gas samples to analyze.

We maintained the hot plate at four temperature ranges for one hour (each): 150–200 °C, 200–250 °C, 250–300 °C and 300–350 °C. A fraction of the vapors formed an organic phase and collected on the surface of the water while the rest was miscible in water. No organic compounds collected in the gas phase of the second vessel.

We contacted both the organic phase and the aqueous phase with toluene and injected 1 μL samples to an Agilent Technologies 7890A GC coupled to an Agilent Technologies 5975C VL mass spectrometer. The GC splitless injector operated at 300 °C. The BR5 GC