Copyrolysis of oxygenate-containing materials with bitumen

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Abstract

Thermal upgrading of bitumen at lower temperature can increase the overall liquid yield, but from a practical point of view, decreasing the temperature leads to lower reaction rate, eroding its industrial value. In order to increase pyrolysis rate at lower temperatures, copyrolysis of bitumen with potentially more reactive oxygenate-containing materials was proposed. The overall aim was to increase liquid yield and decrease gas yield and coke production, while increasing the pyrolysis rate. The oxygenate-containing materials that were investigated were partially oxidized bitumen, coals of different rank (lignite, subbituminous and bituminous) and biomass-derived components (cellulose and lignin). No detectable increase in propagation rate, or decrease in the onset temperature of pyrolysis were observed due to addition of the oxygenate-containg materials. However, synergism with respect to a decrease in gas yield and organic residue was found during copyrolysis with some of the materials. There was meaningful synergism during copyrolysis with bituminous coal and lignin.

Keywords: thermal cracking, oil sands bitumen, coal, biomass, oxidized bitumen, thermogravimetric analysis

Introduction

Canadian oil sands derived bitumen is classified as a heavy oil, with typical density of 1000 kg·m^{-3} (10 °API) and typical viscosity at 60 °C of 10 Pa·s (10 000 cP).(1) Bitumen is therefore not suitable for pipeline transport without upgrading or dilution. There are various processing configurations that can be considered for upgrading of heavy oil.(2) For oil sands derived bitumen, the most economical residue upgrading strategies generally involve delayed coking.(3) This is understandable, since the bitumen has a hydrogen to carbon (H:C) ratio of around 1.5,(1) which is on the low-end of the spectrum for crude oils. Furthermore, the bitumen has a high coking tendency, with typical Conradson carbon residue (CCR) content of 10-14 wt %,(1) as determined by the standard test method ASTM D189.(4) Delayed coking is not only an effective carbon rejection strategy to increase the H:C ratio of the liquid products, but also a strategy to decrease the sulfur and metal content of the liquid products. The coke yield from bitumen pyrolysis is around 20 wt %.(5) This represents a significant mass loss to a product with little commercial value on account of its high sulfur and metals content. The sulfur content of the bitumen is around 5 wt % and the metals (Ni+V) content is in the range 200-300 μg·g^{-1}.(1)

There is economic incentive to improve the liquid yield that can be obtained from delayed coking of bitumen. One way to increase the liquid yield is to perform thermal upgrading at a lower temperature before it is converted by delayed coking. During lower temperature conversion there is a lower probability of over-cracking the lighter liquids to gases. Empirically it is known that thermal cracking at lower temperature also results in less coke formation.(6) Better liquid selectivity is obtained during lower temperature pyrolysis due to the difference in the apparent activation energy between the production of light and potentially gaseous molecules (250 kJ·mol^{-1}) and the production of heavier liquid molecules (230 kJ·mol^{-1}).(7) The problem with pyrolysis at lower temperatures is that the reaction rate halves with approximately every 15 °C decrease in temperature.(7) In order to perform pyrolysis at lower temperatures the reaction rate must be increased, otherwise the process becomes impractical due to the long residence time that will be required.

Copyrolysis of oxygenate-containing materials with bitumen was proposed as a strategy to increase pyrolysis rate at lower temperature and ultimately to also increase liquid yield and decrease gas yield and coke production.

In general C–O bonds have lower bond dissociation energies than C–C and C–H bonds.(8)(9) The decomposition of C–O bonds will enable initiation of pyrolysis (thermal cracking) at lower temperature, which supports the first of our objectives. Low temperature initiation in itself is not sufficient to increase the pyrolysis rate, because pyrolysis rate is mainly determined by the rate of free radical propagation.(10) However, by adding sufficient oxygenate-containing material to the bitumen, it should not only lower the initiation temperature, but also increase the free radical concentration at lower temperatures. It was postulated that an increase in free radical concentration would result in an overall increase in propagation rate. The increased propagation rate at lower temperature would in turn increase in the overall pyrolysis rate.

Our second objective was to increase liquid yield and decrease coke production. This would be a known outcome of lower temperature pyrolysis.(6) Additionally, there may be synergism derived from the copyrolysis of the bitumen with other materials. Of the materials previously considered for copyrolysis with bitumen, bitumen-coal mixtures were the most widely studied.(11)(12)(13)(14)(15)(16)(17)(18)(19)(20) Potential benefits noted in other studies include: processing at lower severity conditions, improved liquid yields, inhibition of coke formation, enhanced demetallation of liquids, reduced raw material input cost and lower capital cost.(14)(15)(16)

In this study the oxygenate-containing materials that were investigated were from three different classes. First was bitumen that was modified by partial oxidation to increase its oxygenate content. Second was coal of three different ranks, namely, lignite, subbituminous and bituminous coal. Third were biomass-derived components, cellulose and lignin.

The study can be divided into two parts. In the first part the pyrolysis behavior of the different raw materials were studied for each material on its own. This provided the baseline for evaluating the anticipated benefits of copyrolysis. The pyrolysis of the raw materials and the copyrolysis of the oxygenate-containing materials with bitumen were studied using mainly two approaches. Thermogravimetric analysis (TGA) with a dynamic change in temperature provided information on the onset temperature of pyrolysis, temperature dependent rate of mass loss and ultimate coke yield. Low temperature pyrolysis was conducted in batch reactors at 380 °C and it provided information on the response of the materials to mild thermal cracking at isothermal conditions. The second part of the investigation dealt with the copyrolysis of oxygenate-containing materials with bitumen. The overall objective was to determine whether there is indeed synergism in copyrolysis, which can lead to higher conversion at lower temperatures, increased liquid yield and decreased production of coke.

Experimental

Materials. Oil sands derived bitumen from Cold Lake (Table 1) was employed. The partially oxidized bitumen (POB) was prepared by exposing the bitumen to the atmosphere while keeping it at 380 °C for 3 hours. An expanded description of the procedure and the equipment employed (Figure S1) can be found in the Supporting Information. The asphaltene fraction from the Cold Lake bitumen employed in this study was obtained by precipitation from a 40:1 *n*-pentane:bitumen mixture after 12 hours of mixing followed by filtration. Three Canadian coals of different ranks were employed, namely, a lignite from Boundary Dam, a subbituminous coal from Coal Valley and a bituminous coal from Teck (Table 2). The cellulose and lignin were commercially obtained from Sigma Aldrich (Table 2): Cotton linters cellulose powder (CAS 9004-34-6) and lignin, kraft (CAS 8068-05-01). The ash-content of the cellulose was < 0.1 wt % and that lignin was 18.2 wt % as determined following the ASTM D3174 standard test method.(21)

Equipment and procedure. Pyrolysis experiments were conducted in small batch micro-reactors that were manufactured from standard 316 stainless steel Swagelok fittings and tubing. The pyrolysis temperature was controlled by submersing the reactors in a temperature controlled fluidized sand bath heater. The heat-up time to reach in internal temperature within 1 °C of the heater temperature is 6 minutes. The batch reactor setup is shown in Figure 1. A more detailed description can be found in the Supporting Information (Figures S2 and S3). For a typical experiment the reactor was loaded with the material (~1 g) to be pyrolyzed and then purged and pressurized to 4 MPa with N_2. The reactor was then submerged in a preheated fluidized sand bath heater (Techne, Model No: SBS-4) at 380 °C for 1 hour, unless otherwise indicated. At the end of the pyrolysis experiment the reactor was removed from the sand bath heater and allowed to cool. The reactor was depressurized and the gas was collected in a gas-bag and analyzed. The remaining liquid was collected and analyzed. The mass of the complete micro-reactor system was recorded after each step using a Mettler Toledo XP1203S (1.2 kg weighing range, with 1 mg readability). This was necessary to determine the gas yield obtained from pyrolysis.

Analyses. TGA to collect mass loss versus temperature data over time was performed using a Mettler Toledo TGA/DSC1 LF FRS2 MX5 with a sample robot. In a typical analysis about 5 mg of sample was placed in a 70 µL alumina (Al_2O_3) pan, which was loaded onto the MX5 balance in the TGA using the sample robot. An open pan was selected to enable fast release of vapor produced during pyrolysis. The balance was allowed to stabilize while under N_2 at a flow rate of 0.33 $mL \cdot s^{-1}$. The analysis was performed over the temperature range 20-900 °C at a constant heating rate of 0.33 $°C \cdot s^{-1}$. Nitrogen flow was maintained during analysis.

Gas analyses were performed using an Agilent 7890A gas chromatograph (GC) with both a flame-ionization detector (FID) and a thermal conductivity detector (TCD). Injection took place through a 6-port sampling valve. Separation was performed using two different columns in the same oven. A molecular sieve column was used for the FID (3 m × 3.2 mm) and a HayeSep R column was used for the TCD (2.4 m × 3.2 mm). The carrier gas was He. The temperature program started at 70 °C and remained at that temperature for 420 s. The temperature was then increased to 250 °C at 0.17 $°C \cdot s^{-1}$ with a hold time of 120 s and then cooled down to 70 °C at -0.5 $°C \cdot s^{-1}$. The column temperature was maintained at 70 °C for 480 s.

Simulated distillation analysis (Sim-Dist) was performed using a Varian 450-GC with a 1093 septum-equipment programmable injector and a CP-8410 autosampler. The injection volume was 0.2 µl. Separation was performed on a Ultimetal Agilent J&W column (5m × 0.53mm). The carrier gas was He. Liquid samples were prepared by dissolving 20-25 mg of the sample in 1.8 g CS_2. The temperature program started at 35 °C and remained at that temperature for 60 s. The temperature was then increased to 400 °C at 0.33 $°C \cdot s^{-1}$ with a hold time of 1545 s.

Results and Discussion

Thermal behavior of raw materials. The thermal behavior of the different raw materials employed in this study was determined by TGA (Figure 2). The accompanying derivative analysis is reported in the Supporting Information (Figure S4). The following observations can be made from these analyses:

(a) The lower rank coals, lignite and subbituminous coal, as well as the biomass component lignin, contain materials that are vaporized in the temperature range below 120 °C. Mass that is lost in this temperature region is usually associated with the loss of water (drying), but the mass loss may also include volatile organic compounds.

(b) The second region of mass loss, 120-230 °C, is characterized by a gradual change in mass. The mass loss is associated with the evaporation of lighter organic compounds from the raw material. It is absent in only three of the raw materials that contains little lighter organic compounds, namely, bituminous coal, cellulose and bitumen derived asphaltenes. Pyrolysis cannot be ruled out and it can take place due to the presence of organic peroxides and other thermally labile functional groups in the raw materials, but pyrolysis is likely a minor contributor to the overall mass loss in this region.

(c) Pyrolysis as a major contributor to mass loss becomes significant in the temperature range 230-350 °C and the inferred onset temperature depends on the material (Table 3). For bitumen and partially oxidized bitumen the starting temperature of this region is not clear, partly because bitumen already contains some lighter products in the atmospheric gas oil range (Table 1). The partially oxidized bitumen nevertheless has a lower inferred onset temperature, as was anticipated. In all of the other materials the inferred onset temperature of pyrolysis is more clearly defined. The inferred onset temperature for the coals follow the anticipated order based on rank, with lignite having the lowest temperature and bituminous coal having the highest temperature. Cellulose is the only material where only one type of linking group is present and once the threshold temperature for pyrolysis is reached, cellulose decomposes completely over a narrow temperature range. This behavior is typical of cellulose.(22)

(d) The temperature range 350-520 °C is typically associated with thermal cracking and all of the raw materials experience meaningful mass loss.
(e) There is a fundamental difference in the coking behavior of bitumen and bitumen derived raw materials on the one hand and lignin and coal on the other hand. Bitumen and bitumen derived materials exhibit little additional mass loss at temperatures above 520 °C. Conversely, lignin and coal continues to pyrolyze and produce lighter products as the temperature is increased up to 900 °C, which was the highest temperature investigated.

Care must be taken not to over-interpret TGA derived data in Table 3. Pyrolysis can take place without mass loss when the products from thermal cracking are not volatile at the temperature where the pyrolysis took place. Conversely, lighter products already present in the raw material can evaporate and will result in mass loss, even though the lighter products were not produced by pyrolysis. Hence, the term inferred onset temperature of pyrolysis is used.

If a mass loss threshold of 5 % is selected to overcome the contribution of volatile products already present, the pyrolysis initiation sequence is: partially oxidized bitumen > raw bitumen > lignin > cellulose > lignite coal ≈ asphaltenes > subbituminous coal > bituminous coal. The coals are in rank order. Based on these results the oxygenate-containing materials did not have lower pyrolysis temperature thresholds than bitumen. It should be noted that oil sands derived bitumen contains a large amount of sulfur (Table 1). The homolytic bond dissociation energies for C–S bonds are consistently lower than that of C–O bonds.(9) The amount of sulfur present in thiol, thioether and disulfide were clearly sufficient to initiate thermal cracking at a lower temperature than possible by oxygenate addition. The only improvement recorded was the slight decrease (<10 °C) in the threshold temperature observed by oxidatively prestressing the bitumen. This is due to the formation of hydroperoxides.(23) The O–O bond in hydroperoxides is weaker than S–S and C–S bonds.(9)

Coke yield of raw materials. The MCR content of petroleum based raw materials can be determined by TGA as described by the standard test method ASTM D4530.(24) The micro carbon residue (MCR) can be related to other measurements of carbon residue that are commonly used to quantify the coking propensity of a material. For bitumen it was reported the

MCR is roughly equal to the CCR, i.e. MCR ≈ CCR.(1) The CCR is a predictor of the coke yield in a delayed coking process and the relationship is given by Equation 1.(25)

Coke yield by delayed coking (wt %) = 1.6 × CCR ... (1)

The raw materials employed in this study were not all of petroleum origin and contained variable amounts of mineral matter. The methodology to determine an organic residue value was adapted to make provision for this. The ash content had to be determined separately, as described by the standard test method ASTM D3174.(21) The ash-contents of the raw materials were reported in the experimental section. An organic residue value on an ash-free basis was determined by TGA (Table 4). The experimental data is provided on an ash-free basis (Equation 2), because most of the feed materials, including bitumen, had some mineral matter present in the feed.

Organic residue (wt %, ash-free) = TGA residue mass (wt %) – Ash content (wt %) ... (2)

Although the organic residue value is not an MCR or fixed carbon value, it is related to these values. The organic residue on ash-free basis provides an indication of the organic product mass that is not recoverable as a liquid or a gaseous product during pyrolysis. Colloquially the organic residue is referred to as coke. However, it should be remembered that for solid raw materials the organic residue contains true coke, a product from hydrogen disproportionation during pyrolysis, as well as unconverted feed.

With the exception of cellulose, all of the oxygenate-containing raw materials had higher organic residue values than bitumen. This was expected, since the other raw materials had lower H:C ratios and higher heteroatom contents than bitumen. Pyrolysis stoichiometry requires that materials with lower H:C ratios produce more coke during pyrolysis and hence have a higher organic residue.

Impact of physical attributes on thermal behavior of raw materials. The particle size distribution and packing density of solid materials affects heat flow and potentially the pyrolysis chemistry. These influences were described in literature.(26)

The raw materials differed in physical form, with bitumen being a viscous liquid, whereas the coals, lignin and cellulose were particulates of non-uniform particle size distributions. The potential impact of the differences in physical attributes of the solid raw materials were determined by pelletizing the powders in a sample press to a pressure of 20 MPa and performing TGA on the pelletized samples (Table 5).

The differences in inferred onset temperature at 5% mass loss between the pelletized and powder samples were 5 °C or less. The temperature values did not show a specific bias, with some pellets having a higher and some having a lower inferred onset temperature. However, the organic residue values displayed a constant bias, with all pelletized samples having a lower organic residue than the powdered samples. The observed effect in the coals was not due to differences in maceral distribution as is usually the case,(28)(29) because the pellets were produced from the powdered coal and not from different size fractions produced by grinding. A plausible explanation is that by increasing the resistance to mass transport for volatile products, the local concentration of compounds capable of hydrogen transfer is increased, which resulted in suppression of coking and ultimately a reduction in the organic residue.(30)

Pyrolysis of raw materials. The thermal behavior of the raw materials obtained by TGA (Figure 2) provided information about the onset of pyrolysis (Table 3) and yield or organic residue (Table 4) under dynamic heating conditions. It was also of interest how these properties of the raw materials were changed during mild pyrolysis at isothermal conditions. The raw materials were therefore subjected to pyrolysis at 380 °C for 1 hour in batch micro-reactors to determine the product yields and gas composition (Table 6).

All pyrolysis experiments were performed in triplicate. The combined liquid and solid product yield is reported. The liquid product was not filtered to determine the coke yield, except for the base case bitumen pyrolysis at 380 °C. The filtered coke yield was 1.4 wt % coke, or 0.6 wt % coke expressed on an ash-free basis. For the 380 °C pyrolyzed bitumen the true liquid yield is 95.6 %, which is close to the liquid+solid yield of 97.0 ± 0.1%. In a related study it was found that bitumen pyrolysis at 400 °C for 1 hour in similar equipment produced <2 wt % coke.(30) In the case of solid raw materials, and materials with significant coke make, the simplification of approximating the liquid and solid product yield to the liquid yield is not valid. However, for solid raw materials it is not possible to differentiate the solids obtained by filtration between coke and unconverted feed material. This is an obstacle often encountered in the conversion of solid raw materials.

The distillation profiles of the raw bitumen samples and the pyrolyzed bitumen provide an indication of the degree of upgrading (Figure 3). This is just an indication of the actual distillation profile and it is likely that some on-column cracking took place during the analysis.(31)

The gaseous product consisted mainly of water, CO_x and light hydrocarbons. The three classes of raw materials produced pyrolysis gas of different compositions. Bitumen and bitumen derived materials produced little pyrolysis gas, and the gas that was produced was rich in hydrocarbons. Coals produced a gaseous product containing mainly water and CO_x. The gas yield decreased with increasing coal rank, with lignite producing most gas and bituminous coal the least gas. The pyrolysis gas from biomass resembled that of coal, but the moisture released by cellulose in particular, was due to progressive dehydration through pyrolysis. At short contact times, as is found in fast pyrolysis, levoglucosan is a major product of cellulose pyrolysis, but if char-forming reactions are allowed to proceed, the main products are water and a carbon-rich char.(32) The products depend on the way in which the oxygen is lost from the cellulose, with loss of water producing polycyclic aromatics, whereas loss as CO_x produces lighter products that contain more hydrogen.(33)

Of all the raw materials pyrolyzed, raw bitumen produced the least amount of pyrolysis gas.

Thermal behavior and coke yield of pyrolyzed materials. TGA (Figure 4) was performed to establish the thermal behavior of the products (liquids and solids) that remained after pyrolysis at 380 °C for 1 hour. This provided information on changes in reactivity of the materials, as well as the yield of organic residue (Table 7). The experimentally measured organic residue will be referred to as a coke yield even though it may include unconverted feed and it was expressed on two different bases. First the coke yield was expressed in terms of the pyrolyzed feed mass loaded in the TGA, which was corrected for the ash content (Equation 2). The ash in the pyrolyzed feed was adjusted based on the change in mass (Equation 3).

Ash in pyrolyzed feed (wt %) = Ash content in raw material feed (wt %) / (Liquid+solids mass fraction from Table 6) ... (3)

The coke yield on the pyrolyzed mass indicated how much of the 380 °C pyrolyzed product was converted into an organic residue by a second more severe pyrolysis conversion. It is a coke yield that is based on only the second pyrolysis conversion, which in these experiments were performed in a thermogravimetric analyzer.

The coke yield was also expressed on the original mass, which is the net coke yield based on the raw material mass after two pyrolysis steps (batch reactor and TGA). This value took the loss of mass to gaseous products during batch reactor pyrolysis into account (Equation 4).

Organic residue on original mass (wt %, ash-free) = TGA residue mass (wt %) × (Liquid+solids mass fraction in Table 6) – Ash content (wt %) ... (4)

The coke yield based on the original mass in Table 7, is therefore different from that in Table 4, which considered coke yield after only one pyrolysis step, instead of two pyrolysis steps. These two values have different meanings. In industrial terms the coke yield in Table 4 gave an indication of the amount of coke produced by converting the raw material under severe conditions in a coking process. The coke yield expressed on original mass in Table 7 gave an indication of the amount of coke produced by a two step process that involved visbreaking at 380 °C for 1 hour followed by coking under severe conditions. The net decrease in solid residue after two pyrolysis steps compared to only a single pyrolysis step is shown in the last column of Table 7.

The following observations were made from these analyses:

(a) The shapes of the mass loss versus temperature data at temperatures above 380 °C were not observably changed by pyrolysis at 380 °C (Figures 2 and 4).

(b) The higher pyrolysis rate at lower temperature that was observed with the partially oxidized bitumen (Figure 2) was lost after pyrolysis (Figure 4). This was expected, since the hydroperoxide O–O bonds that were introduced into the bitumen served as pyrolysis initiators and were converted during pyrolysis at 380 °C.

(c) Pyrolysis at higher temperature resulted in a higher coke yield. Bitumen pyrolyzed at 380 °C produced a lower amount of organic residue than the bitumen pyrolyzed at 390 °C (Table 7). This provided experimental evidence supporting interest in lower temperature pyrolysis, as was noted in the introduction.

(d) The coke yields of the raw bitumen obtained by single-step (Table 4) or two-step pyrolysis (Table 7) were the same within experimental error.

(e) Conversion of coals benefitted from having two pyrolysis steps (Table 7). Unfortunately it is not possible to tell whether the observed decrease in organic residue was due to a decrease in coke formation or an increase in raw material conversion.

(f) Although it was not the purpose to study biomass pyrolysis in particular, these results (Tables 4 and 7) have some implications for biomass pyrolysis processes. It indicates that it is best to separate the cellulose and lignin present in biomass before pyrolysis and pyrolyzing these components separately, because cellulose benefits from single step faster pyrolysis (as simulated by the TGA), whereas lignin benefits from two-step pyrolysis, which includes slower lower temperature pyrolysis.

This concluded the investigation of the pyrolysis behavior of each raw material on its own, thereby establishing the baseline against which copyrolysis can be evaluated.

Thermal behavior and coke yield of raw material mixtures. The evaluation strategy for the mixtures was the same as for the individual raw materials. Mixtures of oxygenate-containing raw materials (10 wt %) and raw bitumen (90 wt %) were prepared. The thermal behavior of the different mixtures was determined by TGA. Visually, the mass loss data for the different mixtures look very similar; the TGA data can be found in the Supporting Information (Figure S5). The yield of organic residue obtained by copyrolysis of the mixtures (Table 8) was compared to the yield of organic residue calculated from the fractional contribution of each raw material (Table 4) under the assumption that there was no synergistic or antagonistic interaction during copyrolysis (Equation 5).

Calculated organic residue (wt %) = 0.9 × Organic residue of bitumen in Table 4 (wt %) + 0.1 × Organic residue of oxygenate-containing raw material in Table 4 (wt %) ... (5)

Potential synergism or antagonism that led to a decrease or increase in organic residue when two materials were copyrolyzed in the TGA, compared to being individually pyrolyzed in the TGA, can be seen in the last column of Table 8. The noticeable differences between the different mixtures were:

(a) The decomposition of the cellulose became apparent at around 360 °C. A maximum increase in mass loss of 5 wt % (absolute) over raw bitumen was observed in the temperature range 390-420 °C. This was less than anticipated from the behavior of cellulose (Figure 2) and suggested that some of the products from cellulose decomposition were incorporated in the liquid product. It did not result in increased pyrolysis of the mixture. Under dynamic heating the effect of cellulose decomposition was fully dissipated at around 490 °C.

(b) The mass loss rate during dynamic heating was similar for all mixtures. There was no observable increase in propagation rate due to the addition of oxygenate-containing materials. This reflected the thermal behavior of the raw materials. As explained before, the C-S and S-S functional groups present in bitumen have lower bond dissociation energies than any of the C-O bonds,(9) and groups containing sulfur, rather than oxygen, dominated the initiation kinetics.

(c) The inferred onset temperature of pyrolysis was not observably decreased by the presence of the oxygenate-containing materials.

(d) A lower amount of organic residue was found for all copyrolyzed mixtures in comparison to the fractional contribution of separate pyrolysis of the raw materials. The exception was the mixture between bitumen and cellulose, which resulted in a higher yield of organic residue.

(e) Copyrolysis of bitumen and bituminous coal resulted in a 6.7 wt % (absolute) lower coke yield (Table 8). This was a clear indication of synergism and it did not fall within the experimental error of the measurements. The synergistic effect of oil sands derived bitumen on bituminous coal dissolution was reported in literature.(17)(18)(20) Apparently this is not a universal effect in coal/oil co-processing. For other heavy oils (Maya, Boscan and North Slope) it was reported that the beneficial effect of co-processing heavy oil and coal is rather weak.(15)

Copyrolysis of bitumen and oxygenate-containing materials. Low temperature copyrolysis of bitumen with oxygenate-containing raw materials was performed in order to amplify any synergistic or antagonistic effects of copyrolysis. Mixtures of oxygenate-containing raw materials (10 wt %) and raw bitumen (90 wt %) were pyrolyzed in batch micro-reactors at 380 °C for 1 hour and the product yields were recorded (Table 9). The gas yields obtained experimentally were also compared to the calculated gas yield from the fractional contribution of each raw material (Table 6) under the assumption that there was no synergistic or antagonistic interaction during copyrolysis (Equation 6).

Calculated gas yield (wt %) = 0.9 × Gas yield of bitumen pyrolysis in Table 6 (wt %) + 0.1 × Gas yield of oxygenate-containing raw material pyrolysis in Table 6 (wt %) ... (6)

Compared to the gas yield of 3.0 ± 0.1 wt % obtained during pyrolysis of bitumen on its own at 380 °C for 1 hour (Table 6), copyrolysis with partially oxidized bitumen, subbituminous coal and bituminous coal resulted in similar or lower gas yields (Table 9). Furthermore, in all instances the actual gas yields during copyrolysis were lower than the gas yields calculated from the fractional contribution of each raw material (Table 6) under the assumption that there was no interaction during copyrolysis. In fact, the relative decrease in gas yield ranged from 10 % for lignin to 30 % for bituminous coal.

To get an indication of the solids fraction in the combined liquid+solid product, the yield of solid residue was determined by filtration for selected samples (Table 9). It was found that the copyrolysis of bitumen with partially oxidized bitumen resulted in a coke yield of 11.7 wt %, or 11.1 wt % on an ash-free basis. It is likely that much of this is due to the increased asphaltene content,(34) which led to increased asphaltene precipitation in addition to coking. The relative contributions of each were not resolved in this study. Irrespective, it constituted a meaningful decrease in liquid yield. Conversely, the yield of solid residue obtained during copyrolysis with bituminous coal was 2.7 wt %, or 1.0 wt % on an ash-free basis. Thus, most of the bituminous coal was liquefied, because the coke yield of bitumen on its own (Table 6) was 0.6 wt % on an ash-free basis. The solid residue from cellulose copyrolysis was 3.5 wt %, or 2.8 wt % on an ash-free basis.

Evidence of synergism was also observed in the lower organic residue values that were obtained by TGA performed after copyrolysis of bitumen with some of the oxygenate-containing additive materials (Table 10). The organic residue values are for a two-step pyrolysis conversion, first in a batch reactor and then in the TGA. As explained before, this mimics a low temperature visbreaking process followed by severe coking.

Subbituminous coal, bituminous coal and lignin had lower amounts of organic residue during copyrolysis with bitumen than would have been obtained had these materials been pyrolyzed individually. However, it should be pointed out that the benefit derived from copyrolysis with subbituminous coal is not conclusive, because it was within the experimental error. Conversely, copyrolysis of bitumen with cellulose was detrimental and the yield of organic residue increased. The copyrolysis of partially oxidized bitumen did not affect the yield of organic residue, which suggest that most of the coke that was found by filtration (Table 9) was due to asphaltene precipitation. Copyrolysis with lignite coal seemed detrimental to the yield of organic residue, but the difference was within experimental error.

The synergism during copyrolysis of bituminous coal with bitumen, resulted in lower coke and gas yields than could be obtained by separate pyrolysis of these materials. These observations supported previous reports in literature on co-processing bitumen and bituminous coal.(20) The reason for this synergism is not clear. A seemingly obvious explanation is that bitumen acts as solvent to facilitate coal swelling and hydrogen transfer, but the work of Siskin and Scouten(35) indicated that the role of bitumen (albeit coal derived in their study) is not necessary beneficial for coal dissolution, or any of the reasons postulated. Another possible explanation is that the bitumen facilitates more effective hydrogen disproportionation, as was observed in the results of Szuba and Michalik.(19) The high content of naphthenic-carbon in bitumen,(36) makes bitumen a typical hydrogen donor solvent for coal liquefaction. Whatever the reason, the present investigation only provided evidence of synergism and not evidence favoring a specific explanation of the synergism.

The liquid product profiles of the copyrolysis products were compared to that obtained by bitumen pyrolysis without additives (Table 11). The liquid product distribution was determined by simulated distillation and care must be taken with the interpretation, because some on-column cracking could have taken place.(31) Furthermore, it is important to note that the residue fraction cannot be completely converted into heavy products. With severe pyrolysis, as simulated by TGA, the ultimate calculated conversion based on the organic residue (Table 10) and ash content of the feed is indicated in the last column of Table 11.

Conclusions

The objective of the investigation was to determine whether there is synergism in copyrolysis, which can lead to higher conversion at lower temperatures, increased liquid yield and decreased gas yield and production of coke. Synergism was found during copyrolysis of some oxygenate-containing materials with bitumen. The following conclusions and observations were made:

(a) Oil sands derived bitumen inherently has a low initiation temperature for thermal conversion. The addition of oxygenate-containing materials did not decrease the temperature threshold for pyrolysis. A marginal decrease (less than 10 °C) in the temperature threshold for pyrolysis could be achieved by oxidative prestressing of the bitumen, which introduced more labile peroxy groups into the bitumen.

(b) The initiation kinetics of bitumen and mixtures containing bitumen was dominated by the pyrolysis of C–S (thiol, thioether) and S–S bonds in the bitumen. These bonds have lower bond dissociation energies than C–O bonds.

(c) Bitumen is a superior low temperature (380 °C) pyrolysis feed when compared to the oxygenate-containing raw materials. Bitumen had the second lowest organic residue (13 wt %, ash-free), with only cellulose having a lower yield of organic residue. Bitumen also produced the least amount of pyrolysis gas (3 wt %).

(d) Low temperature pyrolysis at 380 °C for 1 hour followed by severe pyrolysis in the TGA, compared to just severe pyrolysis in the TGA affected the amount of organic residue that was produced by the raw materials differently. Within experimental error, the two-step pyrolysis had little effect on the coke yield of bitumen, it decreased the coke yield of all ranks of coal and lignin, and it increased the coke yield of partially oxidized bitumen and cellulose.

(e) Biomass pyrolysis processes can be improved by separating the cellulose and lignin present in the biomass before pyrolysis and pyrolyzing these components separately. Cellulose benefits from single step pyrolysis, whereas lignin benefits from two-step pyrolysis that includes slower lower temperature pyrolysis.

(f) The benefit of pyrolyzing bitumen at lower temperature was confirmed. The gas yield and coke yield of bitumen pyrolyzed at 380 °C for 1 hour was lower than that of bitumen pyrolyzed at higher temperatures. Furthermore, the < 566 °C liquid yield obtained was similar, even though the product from higher temperature pyrolysis was overall lower boiling.

(g) Copyrolysis under dynamic heating conditions decreased the micro-carbon residue coke yield of most mixtures beyond that of separate pyrolysis of the raw materials. This was particularly evident during copyrolysis of bitumen and bituminous coal, which resulted in a 6.7 wt % (absolute) lower coke yield.

(h) Under isothermal conditions, 380 °C for 1 hour, copyrolysis of bitumen (90 wt %) and oxygenate-containing additives (10 wt %) was synergistic and resulted in lower gas yields than would have been obtained had these materials been pyrolyzed individually. In the case of bituminous coal, the absolute gas yield was also meaningfully lower.

(i) The yield of organic residue was meaningfully lower during isothermal copyrolysis at 380 °C only for bitumen mixtures containing bituminous coal and lignin when compared to the calculated amount of organic residue expected for separate pyrolysis of these materials.

Supporting Information Available: An expanded description of the procedure and equipment (Figure S1) used to prepare the POB is provided. The equipment (Figures S2 and S3) and procedure for pyrolysis experiments are also described in more detail. The derivative analysis of the TGA data of the raw materials is shown (Figure S4), as well as the TGA of the raw material mixtures (Figure S5). A more detailed analysis of the gases from pyrolysis of raw materials and mixtures are provided (Tables S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Characterization of Cold Lake oil sands derived bitumen and partically oxidized bitumen employed in this study.

Description	Cold Lake bitumen	Partially oxidized bitumen
Elemental analysis (wt %)		
carbon	84.1	84.1
hydrogen	10.0	10.0
nitrogen	0.6	0.6
sulfur	5.3	4.6
oxygen (by difference)	0.0	0.7
Ash content (wt %)	0.7	0.7
Higher heating value (MJ·kg^{-1})	41.6	41.5
Asphaltene content (wt %)	19.3	
Distillation profile (wt %)		
light naphta (40-79 °C)	<1	
heavy naphta (79-191 °C)	<1	
kerosene (191-277 °C)	<1	
atmospheric gas oil (277-343 °C)	6	
vacuum gas oil (343-566 °C)	42	
vacuum residue (>566 °C)	~50	

Table 2. Characterization of Canadian coals and biomass components employed in this study.

Description	Lignite	Subbituminous coal	Bituminous coal	Cellulose	Lignin
Origin	Boundary Dam	Coal Valley	Teck	Sigma-Aldrich	Sigma-Aldrich
Proximate analysis (wt %) [a]					
moisture	1.3	5.5	1.9		
ash [b]	15.3	12.4	10.5	< 0.1	18.2
volatile matter	39.0	31.4	24.6		
fixed carbon	44.4	50.7	63.0		
Ultimate analysis (wt %)					
carbon	58.6	65.4	84.3	43.7	49.1
hydrogen	4.3	4.2	4.6	6.0	4.7
nitrogen	1.3	0.8	1.4	0.0	0.1
sulfur	0.8	0.4	0.7	0.1	4.4
oxygen (by difference)	35.1	29.2	9.0	50.2	41.7
Higher heating value ($MJ\cdot kg^{-1}$)	21.6	24.5	33.7	17.1	18.4

[a] Coals were dried under vacuum before analysis.

[b] Sample to sample variations of ± 2 wt % (absolute) were found during repeat analyses of ash content.

Table 3. The inferred onset temperature for pyrolysis for the raw materials employed in this study.

Material	Temperature at threshold mass loss (°C) [a]		
	1 %	5 %	10 %
Bitumen			
raw bitumen	255	276	297
partially oxidized bitumen	254	268	286
asphaltenes	290	377	416
Coal			
lignite	289	372	424
subbituminous coal	328	421	461
bituminous coal	419	479	516
Biomass			
cellulose	304	333	340
lignin	262	296	322

[a] The inferred onset temperature is defined based on the mass loss relative to the sample mass at 250 °C. This does not rule out the contribution of compounds with boiling points of >250 °C that are already present in the raw material.

Table 4. Organic residue of raw materials on an ash-free basis.

Material	Organic residue (wt %, ash-free) [a]
Bitumen	
raw bitumen	13.3 ± 0.2
partially oxidized bitumen	19.6 ± 0.6
asphaltenes	39
Coal	
lignite	42.6 ± 0.8
subbituminous coal	56.2 ± 0.4
bituminous coal	69.5 ± 0.2
Biomass	
cellulose	8.7 ± 0.5
lignin	32.4 ± 1.7

[a] Uncertainty in experimental values are expressed as sample standard deviations.

Table 5. Temperature threshold for pyrolysis mass loss and organic residue on an ash-free basis for pelletized raw materials.

Pelletized material	Temperature at threshold mass loss (°C) [a]			Organic residue (wt %, ash-free)	Difference: Pellets – powder [b]	
	1%	5%	10%		5% mass loss (°C)	coke (wt %, ash-free)
Coal						
lignite	287	374	429	38.3	2	-4.3
subbituminous coal	324	423	462	54.4	2	-1.8
bituminous coal	388	475	510	66.4	-5	-3.1
Biomass						
cellulose	308	333	341	6.8	0	-1.8
lignin	266	299	327	28.0	3	-4.4

[a] Mass loss calculated relative to mass at 250 °C (see Table 3).

[b] Tables 3 and 4 contain the results for raw materials in powdered form.

Table 6. Product yields and composition of the gaseous product from the batch reactor pyrolysis of materials at 380 °C and 1 hour.

Pyrolyzed material	Yield (wt %)		Standard deviation (%)	Gas composition (mol %, water-free)					
	liquid + solid	gas		C_1	C_2	C_3-C_4	C_5+	CO	CO_2
Bitumen									
bitumen	97.0 [a]	3.0	0.1	19	12	14	30	12	13
bitumen (390 °C) [b]	96.0	4.0	0.5	29	9	13	23	10	16
partially oxidized bitumen	94.5	5.5	0.3	10	2	5	13	29	41
Coal									
lignite	77.2	22.8	0.4	3	<1	<1	1	12	83
subbituminous coal	87.0	13.0	0.3	4	1	1	1	20	73
bituminous coal	92.4	7.6	0.7	3	1	1	1	27	68
Biomass									
cellulose [c]	27.6	72.4	6.2	13	5	1	9	22	47
lignin	73.6	26.4	0.8	8	1	<1	1	13	78

[a] Coke yield by filtration is 1.4 wt % (0.6 wt % on an ash-free basis).

[b] Pyrolysis was conducted at 390 °C for 1 hour instead of 380 °C.

[c] Oxygenates present; gas composition does not add up to 100 %.

Table 7. Organic residue of raw materials on an ash-free basis, expressed in terms of the pyrolyzed sample mass and the original raw material mass before pyrolysis.

Pyrolyzed material	Organic residue (wt %, ash-free)		
	on pyrolyzed mass [a]	expressed on original mass basis	change relative to Table 4 [b]
Bitumen			
bitumen	15.0 ± 0.7	14.6	1
bitumen (390 °C) [c]	19.0 ± 1.1	18.3	-1
partially oxidized bitumen	31.4 ± 0.9	29.7	-9
Coal			
lignite	47.5 ± 0.5	36.7	-6
subbituminous coal	61.1 ± 0.4	53.2	-3
bituminous coal	71.5 ± 0.9	66.0	-3
Biomass			
cellulose	70.5 ± 1.2	19.4	11
lignin	38.4 ± 0.8	28.3	-4

[a] Uncertainty in experimental values are expressed as sample standard deviations.

[b] Negative values imply that two pyrolysis steps in series lead to less organic residue.

[c] Pyrolysis was conducted at 390 °C for 1 hour instead of 380 °C.

Table 8. Organic residue (coke) on an ash-free basis of mixtures containing 90 wt % bitumen and 10 % wt additive material.

Additive material	Organic residue (wt %, ash-free)		
	experimental	calculated [a]	synergy [b]
Bitumen			
partially oxidized bitumen	12.9 ± 0.5	13.9	-1
Coal			
lignite	15.8 ± 0.5	16.2	-0.4
subbituminous coal	14.8 ± 1.2	17.6	-3
bituminous coal	12.2 ± 0.1	18.9	-7
Biomass			
cellulose	13.3 ± 0.2	12.8	0.5
lignin	13.6 ± 0.6	15.2	-2

[a] Calculated from the fractional contribution of the raw materials (Table 4) to the organic residue, which assumed that there was no interaction between the materials during pyrolysis.

[b] Negative values imply that copyrolysis leads to less organic residue.

Table 9. Product yields and composition of the gaseous product from the batch reactor copyrolysis of 90 wt % bitumen and additive material mixtures at 380 °C for 1 hour.

Additive material	Yield (wt %)			Standard deviation (%)	Gas composition (mol %, water-free)					
	liquid + solid	gas	calculated gas [a]		C_1	C_2	C_3-C_4	C_5+	CO	CO_2
Bitumen										
partially oxidized bitumen	97.2 [b]	2.8	3.3	0.2	23	12	13	29	9	14
Coal										
lignite	96.1	3.9	5.0	0.3	18	9	8	16	5	45
subbituminous coal	97.1	2.9	4.0	0.2	25	13	10	16	9	28
bituminous coal	97.7 [c]	2.3	3.5	0.5	23	12	12	24	12	19
Biomass										
cellulose	92.2 [d]	7.8	9.9	0.5	15	8	6	10	19	43
lignin	95.3	4.8	5.3	0.5	23	9	7	13	8	40

[a] Calculated from the fractional contribution of the raw materials (Table 6) to the gas yield, which assumed that there was no interaction between the materials during pyrolysis.

[b] Coke yield by filtration is 11.7 wt % (11.1 wt % on an ash-free basis).

[c] Organic residue yield by filtration is 2.7 wt % (1.0 wt % on an ash-free basis).

[d] Organic residue yield by filtration is 3.5 wt % (2.8 wt % on an ash-free basis).

Table 10. Organic residue (coke) on an ash-free basis from the batch reactor copyrolysis of 90 wt % bitumen and additive material mixtures at 380 °C for 1 hour.

Additive material	Organic residue (wt %, ash-free)			
	on pyrolyzed mass	expressed on original mass basis	calculated [a]	synergy [b]
Bitumen				
partially oxidized bitumen	16.5 ± 0.7	16.1	16.1	~0
Coal				
lignite	18.0 ± 1.3	17.3	16.8	0.5
subbituminous coal	18.3 ± 1.0	17.7	18.4	-0.7
bituminous coal	15.7 ± 0.9	15.3	19.7	-4
Biomass				
cellulose	19.9 ± 1.7	18.3	15.1	3
lignin	13.7 ± 0.5	13.1	15.9	-3

[a] Calculated from the fractional contribution of the pyrolyzed raw materials (Table 7) to the organic residue, which assumed that there was no interaction between the materials during pyrolysis.

[b] Negative values imply that copyrolysis leads to less organic residue.

Table 11. Product profiles of pyrolyzed bitumen and bitumen copyrolyzed with oxygenate-containing additives at 380 °C for 1 hour.

Additive material	Product distribution (wt %)						Ultimate conversion (wt %, ash-free) [a]
	gas	naphtha, <191 °C	kerosene, 191-277 °C	atmospheric gas oil 277-343 °C	vacuum gas oil 343-566 °C	residue	
Bitumen							
none (bitumen only)	3	1	3	7	41	45	85.4
partially oxidized bitumen	3	3	4	10	44	36	83.9
Coal							
lignite	4	2	3	8	42	40	82.7
subbituminous coal	3	4	5	9	44	36	82.3
bituminous coal	2	2	3	6	34	53	84.7
Biomass							
cellulose	8	4	6	9	52	22	81.7
lignin	5	3	4	9	42	38	86.9

[a] Total conversion of organic matter to lighter, non-solid products that is possible after severe pyrolysis.

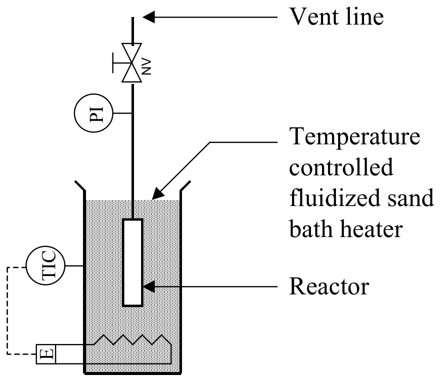

Figure 1. Batch reactor setup employed in pyrolysis experiments.

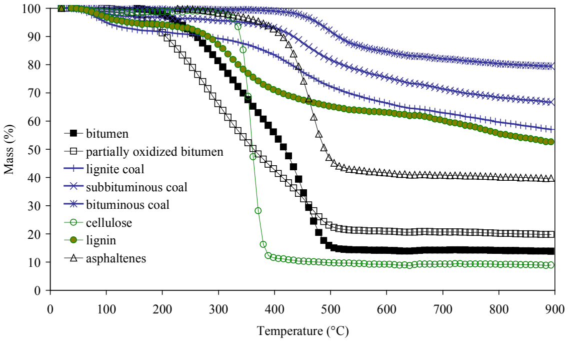

Figure 2. TGA of raw materials over the range 20-900 °C performed under N_2 flow rate of 0.33 mL·s^{-1} and at a heating rate of 0.33 °C·s^{-1}.

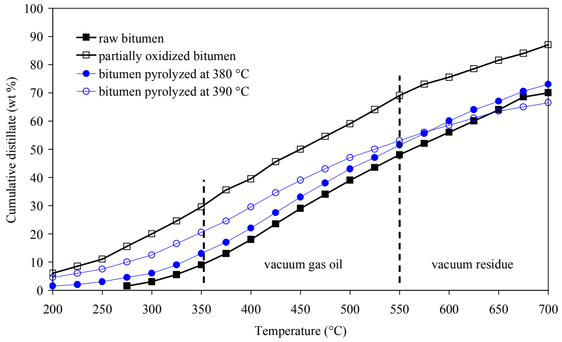

Figure 3. Simulated distillation of bitumen, partially oxidized bitumen and the liquid products from bitumen pyrolysis at 380 °C and 390 °C for 1 hour.

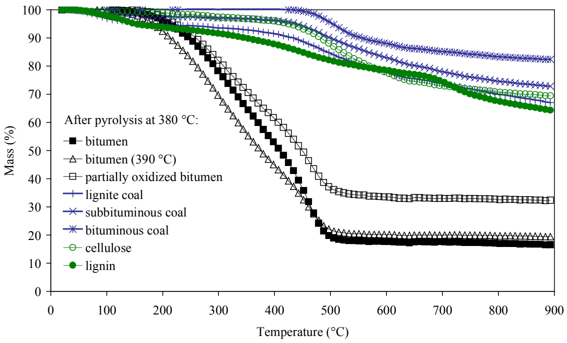

Figure 4. TGA of pyrolyzed materials produced by thermal conversion in a batch reactor at 380 °C for 1 hour. TGA conducted over the range 20-900 °C under N_2 flow rate of 0.33 mL·s^{-1} and at a heating rate of 0.33 °C·s^{-1}.