

SUPPORTING INFORMATION:

Copyrolysis of oxygenate-containing materials with bitumen

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Introduction

It was our intent to report the work with sufficient clarity and detail so that the main paper is complete and can be read on its own. The purpose of this document is to provide non-essential, albeit useful, additional information that supports the main paper. The following aspects are covered in this document:

- (a) A more elaborate description of the preparation procedure for partially oxidized bitumen (POB), which was employed as a raw material in the copyrolysis studies.
- (b) The equipment and procedure employed during pyrolysis is described in more detail.
- (c) Derivative analysis of mass loss regions observed in the temperature range 20-900 °C.
- (d) Analysis of the pyrolysis gases produced during the conversion of the raw materials and mixtures of bitumen with oxygenate-containing additives.
- (e) Thermal behavior of mixtures of bitumen with oxygenate-containing additives under dynamic heating during TGA.

Experimental

Preparation of partially oxidized bitumen (POB). Cold Lake bitumen (1 g) was added to a micro reactor. The micro reactor was sealed by a lid and attached to a tube ([Figure S1](#)). The reactor and tubing were constructed from 316 stainless steel using standard Swagelok fittings. The whole system was held in place using a clamp. The outlet of tubing was placed in a fume

hood to limit fugitive emissions in the laboratory. The reactor and a small part of the tube were put inside a preheated sand bath at 380 °C and remained in the sand bath for three hours. The reactor was not purged with N₂, nor was it closed off from the atmosphere. Thus, even though it was not supplied with flowing air, O₂ from the atmosphere could enter the system. After three hours, the system was taken out and allowed to cool down to the room temperature.

Pyrolysis experiments. About 1g of bitumen was added to a micro reactor. For the copyrolysis experiments the oxygenate-containing additive material was added to yield a 9:1 mass ratio of bitumen:additive, i.e. 10 wt % additive in the mixture. The micro reactor is shown in [Figure S2](#). Its capacity is 15 mL and the internal diameter is 10 mm. The reactor was closed by hand, only loosely, just to measure the initial weight of the whole system (W₁) before purging it with N₂. After purging the reactor was pressurized to 4 MPa and a leak test was performed. Once the system passed the leak test the reactor was weighed again (W₂). The mass of the N₂ added could thus be calculated (W₂-W₁). A Mettler Toledo XP1203S with 1.2 kg weighing range and 1 mg readability was employed, so that the mass of the complete micro-reactor system could be determined to 1 mg accuracy. This was found to be the most accurate way to determine yields for such small samples.

For the pyrolysis experiment the micro reactor was attached to a clamp and it was placed inside a preheated sand bath ([Figure S3](#)). Each pyrolysis experiment lasted one hour and the temperature in the sand bath was 380 °C unless otherwise indicated. The temperature of the sand bath was controlled, not that of the micro-reactor. It is known from temperature calibrations that it takes 5-6 minutes for the internal temperature in the micro-reactor to reach 380 °C.

After pyrolysis the reactor was removed and allowed to cool down. After the reactor was completely cooled, the system was cleaned to remove any sand that may have stuck to the reactor. The mass of the system was recorded (W₃). This measurement was employed to check that no leaks developed during pyrolysis ([Equation S1](#)).

$$\left| \frac{W_3 - W_2}{W_2 - W_1} \right| < 0.01 \quad \dots (S1)$$

A gas-bag was attached to the system to collect the produced gases, as well as the N₂ used to pressurize the system. The gas-bag was connected to the system by clear tubing and to avoid gas leakage during the collection, some Teflon tape (PTFE tape) was used to tighten the part of the attachment of the tube to the gas-bag. For the other end of the tube which is connected to the reactor system, a nut and ferrule was used. The gas that was collected in the gas-bag was analyzed by gas chromatography. The liquid product was collected and analyzed in different ways as described in the main paper. The masses of all samples were recorded in order to perform a material balance.

Results and Discussion

Thermal behavior of raw materials. The derivative analysis (Figure S4)⁽¹⁾ of the TGA mass loss data of the raw materials provides a graphic illustration of the main regions of mass loss:

- (a) Region 1: The mass loss <120 °C is associated with water loss.
- (b) Region 2: Some product distillation takes place, but generally mass loss is minor in the range 120-230 °C.
- (c) Region 3: In the temperature range 230-350 °C product distillation becomes more significant for the bitumen and bitumen-derived materials. This is also the region where onset of pyrolysis occurs (even though initiation of pyrolysis may take place at lower temperatures, especially in the presence of peroxides and other very labile compounds). In the case of bitumen there is about 6 % of the raw material with a boiling point in the atmospheric gas oil (277-343 °C) range and that will distill in this region and <1 % with a boiling point <277 °C (Table 1). Hence the use of the 5 % mass loss about 250 °C criterion to determine the inferred onset of pyrolysis (Table 3).
- (d) Region 4: Thermal cracking actively takes place in the 350-520 °C.
- (e) Region 5: Only the coals and lignin show meaningful further mass loss >520 °C, but the rate is low.

Pyrolysis of raw materials. The pyrolysis gases from the pyrolysis of the raw materials at 380 °C were analyzed by gas chromatography (Table S1).⁽¹⁾ The sample standard deviations were calculated from experiments performed in triplicate.

A calibration gas was employed to calculate appropriate response factors for both the flame ionization detector (FID) and thermal conductivity detector (TCD). The response factors for the FID included the molar mass of the compounds, so that the values are in molar concentrations.

The water content of the pyrolysis gas was not properly quantified, which is an unfortunate deficiency of the gas analyses. The composition is therefore provided on a water-free basis. There was moisture present in the coal samples; water was also released during pyrolysis of the coal and biomass samples.

Thermal behavior of raw material mixtures. The TGA for the mixtures of 90 wt % bitumen with 10 wt % oxygenate containing compounds is shown in Figure S5.⁽¹⁾ There is very little difference between the different samples.

Copyrolysis of bitumen and oxygenate-containing materials. The pyrolysis gases produced during the pyrolysis of the bitumen and oxygenate-containing additive mixtures were analyzed by gas chromatography (Table S2).⁽¹⁾ The sample standard deviations were calculated from experiments performed in triplicate.

Acknowledgements

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Literature cited

- (1) Toosi, E. Copyrolysis of bitumen and oxygenate containing materials at low temperature. MSc thesis, University of Alberta, Edmonton, AB, Canada, 2013.

Table S1. Chromatographic analysis of the pyrolysis gases produced during pyrolysis of raw materials in batch micro-reactors at 380 °C and 4 MPa N₂ pressure for 1 hour. The gas concentrations are on a water-free molar basis. The standard deviation (SD) of experiments in triplicate is indicated.

Compound	Composition (mol %)							
	bitumen	bitumen	partially	lignite	subbitu-	bitu-	cellulose	lignin
	(390 °C)	oxidized			minous	minous	^b	
	^a	bitumen			coal	coal		
CH ₄ (methane)	19.36	29.36	9.86	2.74	3.76	3.26	13.11	8.08
SD CH ₄	5.02	7.60	0.75	0.37	0.97	0.54	0.51	0.63
C ₂ H ₄ (ethylene)	1.12	0.75		0.29	0.41		0.76	0.10
SD C ₂ H ₄	0.26	0.54		0.04	0.06		0.03	0.15
C ₂ H ₆ (ethane)	10.65	7.77	2.06		0.51	0.59	4.19	0.46
SD C ₂ H ₆	2.04	5.55	2.06		0.04	0.59	0.26	0.35
C ₃ H ₆ (propylene)	1.00	0.00						
SD C ₃ H ₆	1.25	0.00						
C ₃ H ₈ (propane)	3.32	2.22	1.88	0.05	0.26	0.25	0.01	0.14
SD C ₃ H ₈	2.56	0.93	0.17	0.08	0.02	0.18	<0.01	0.09
C ₄ H ₁₀ (i-butane)	1.32	1.94					0.64	0.10
SD C ₄ H ₁₀	0.45	0.76					0.04	0.13
C ₄ H ₁₀ (<i>n</i> -butane)	7.86	8.17	1.72	0.11	0.24	0.21	0.02	0.06
SD C ₄ H ₁₀	2.18	2.90	0.09	0.07	0.10	0.02	0.01	0.06
C ₄ H ₈ (butenes)	0.72	0.53	1.68	0.09	0.11	0.21	0.00	0.05
SD C ₄ H ₈	0.15	0.06	1.33	0.06	0.11	0.07	<0.01	0.01
C ₅ H ₁₂ (i-pentane)	7.66	5.29	2.82	0.38	0.12	0.50	2.74	0.10
SD C ₅ H ₁₂	2.24	1.45	0.35	0.18	0.10	0.11	0.00	0.02
C ₅ H ₁₂ (<i>n</i> -pentane)	20.41	17.42	7.93	0.30	1.11	0.00	5.73	0.32
SD C ₅ H ₁₂	4.63	5.38	0.81	0.30	0.23	0.00	3.93	0.24
C ₆ H ₁₂ (hexenes)	0.85		1.70	0.02	0.04	0.19	0.21	0.17
SD C ₆ H ₁₂	0.52		0.18	0.01	0.03	0.01	<0.01	0.05

C ₆ H ₁₄ (<i>n</i> -hexane)	0.84	0.57	0.32	0.03	0.07		0.11	
SD C ₆ H ₁₄	0.42	0.21	0.02	0.04	0.06		<0.01	
CO (carbon monoxide)	12.00	10.16	29.13	12.49	20.21	26.67	22.32	12.56
SD CO	1.97	3.79	0.76	0.01	2.19	2.55	9.51	2.59
CO ₂ (carbon dioxide)	12.93	15.80	40.89	82.84	73.16	68.11	46.66	77.83
SD CO ₂	0.74	9.30	2.05	1.16	1.64	1.01	1.34	1.25

^a Pyrolysis was conducted at 390 °C for 1 hour instead of 380 °C.

^b Oxygenates present; gas composition does not add up to 100 %.

Table S2. Chromatographic analysis of the pyrolysis gases produced during copyrolysis of mixtures containing 90 wt % bitumen and additive raw materials in batch micro-reactors at 380 °C and 4 MPa N₂ pressure for 1 hour. The gas concentrations are on a water-free molar basis. The standard deviation (SD) of experiments in triplicate is indicated.

Compound	Composition (mol %)					
	10 % partially oxidized bitumen	10 % lignite	10 % subbitu- minous coal	10 % bitu- minous coal	10 % cellulose	10 % lignin
CH ₄ (methane)	22.52	17.90	24.70	22.99	15.17	22.51
SD CH ₄	0.84	1.11	1.79	0.96	0.48	3.06
C ₂ H ₄ (ethylene)	1.17	0.48	0.72	0.37	0.56	0.84
SD C ₂ H ₄	0.09	0.34	5.11	0.53	0.40	0.19
C ₂ H ₆ (ethane)	10.56	8.13	12.13	11.14	7.46	8.10
SD C ₂ H ₆	0.51	0.79	0.88	0.53	0.38	0.53
C ₃ H ₆ (propylene)	1.20			1.14		
SD C ₃ H ₆	1.70			0.24		
C ₃ H ₈ (propane)	5.24	0.86	1.24	1.14	0.76	0.89
SD C ₃ H ₈	2.91	0.02	0.03	0.24	0.07	0.08
C ₄ H ₁₀ (i-butane)	0.43	1.08	1.47	1.19	0.82	0.95
SD C ₄ H ₁₀	6.04	0.16	0.09	0.33	0.11	0.05
C ₄ H ₁₀ (<i>n</i> -butane)	6.03	5.23	6.49	7.78	3.92	4.77
SD C ₄ H ₁₀	0.10	0.53	0.15	0.62	0.33	0.12
C ₄ H ₈ (butenes)	0.59	0.39	0.50	0.59	0.35	0.43
SD C ₄ H ₈	<0.01	0.04	0.08	0.23	0.03	0.04
C ₅ H ₁₂ (i-pentane)	6.85	3.33	3.69	4.57	2.10	2.88
SD C ₅ H ₁₂	0.29	0.36	0.14	0.07	0.24	0.37
C ₅ H ₁₂ (<i>n</i> -pentane)	20.82	11.90	11.45	18.37	7.22	9.63
SD C ₅ H ₁₂	0.80	1.41	0.53	2.82	1.10	1.38
C ₆ H ₁₂ (hexenes)	0.61	0.54	0.53	0.69	0.21	0.39

SD C ₆ H ₁₂	0.56	0.05	0.05	0.09	0.03	0.10
C ₆ H ₁₄ (<i>n</i> -hexane)	1.00	0.53	0.47	0.82	0.30	0.41
SD C ₆ H ₁₄	0.41	0.07	0.02	0.23	0.06	0.09
CO (carbon monoxide)	8.82	4.52	8.74	11.84	18.50	7.73
SD CO	3.06	1.73	0.92	1.53	1.47	1.62
CO ₂ (carbon dioxide)	14.14	45.12	27.84	18.50	42.63	40.46
SD CO ₂	3.07	3.44	1.45	2.09	1.29	2.70

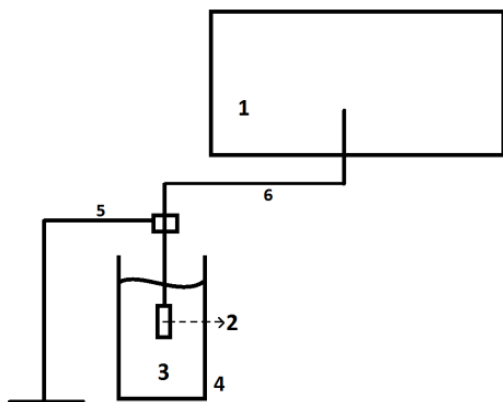


Figure S1. Experimental setup for the preparation of the partially oxidized bitumen sample. The equipment shown are: 1 - fume hood, 2 - micro reactor, 3 - sand, 4 - sand bath, 5 - clamp, and 6 – tubing.

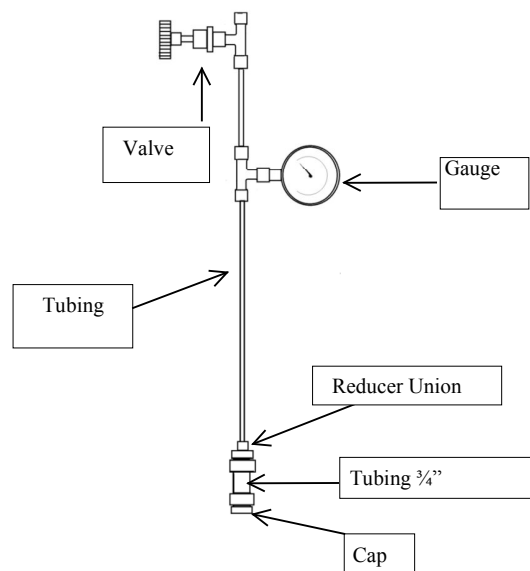


Figure S2. Design details of the micro-reactor employed in pyrolysis experiments.

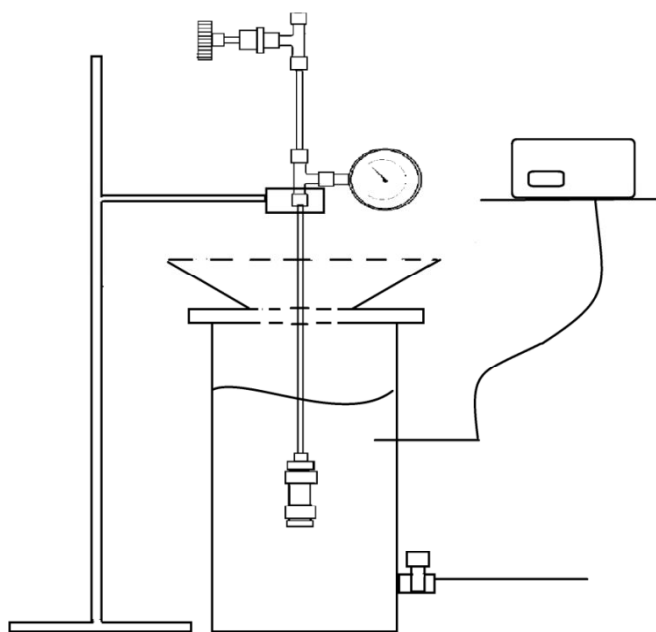


Figure S3. Experimental setup used for pyrolysis experiments.

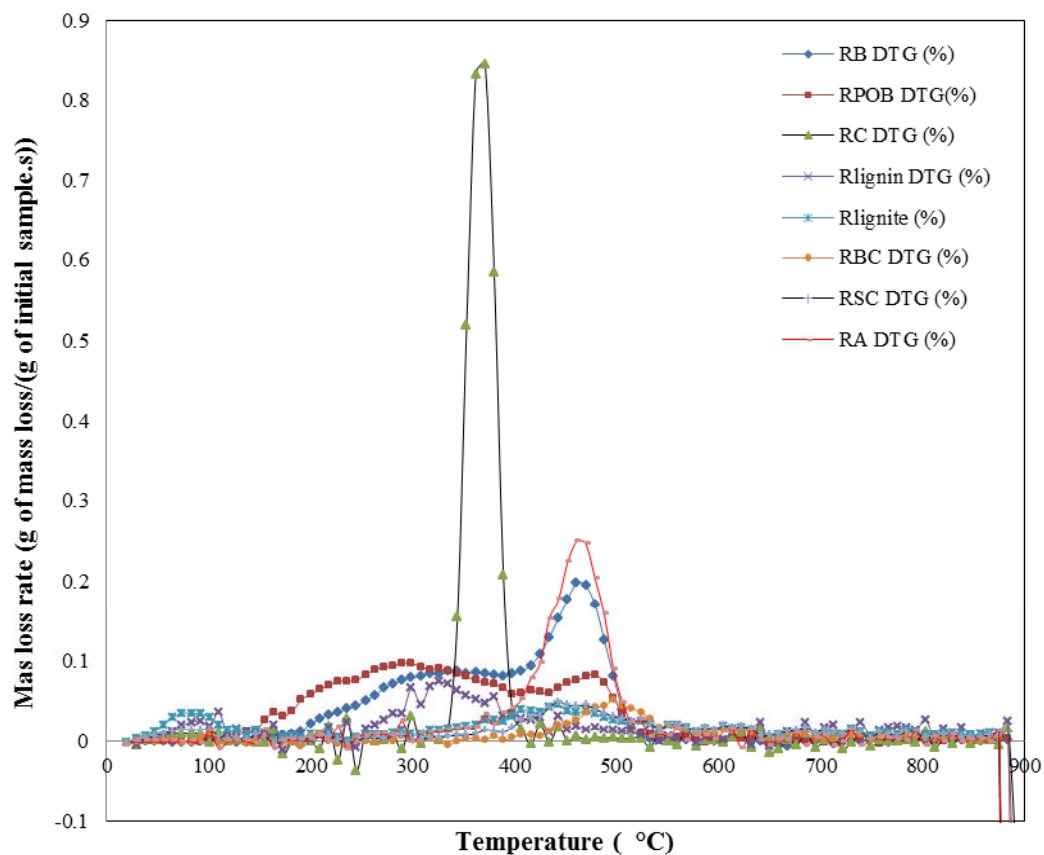


Figure S4. First derivative of the relative mass loss over time shown in Figure 1. TGA of the raw materials were conducted over the range 20-900 °C under N_2 flow rate of $0.33 \text{ mL}\cdot\text{s}^{-1}$ and at a heating rate of $0.33 \text{ }^\circ\text{C}\cdot\text{s}^{-1}$. The raw materials analyzed were: bitumen (RB), partially oxidized bitumen (RPOB), asphaletens (RA), lignite coal (Rlignite), subbituminous coal (RSC), bituminous coal (RBC), cellulose (RC) and lignin (Rlignin).

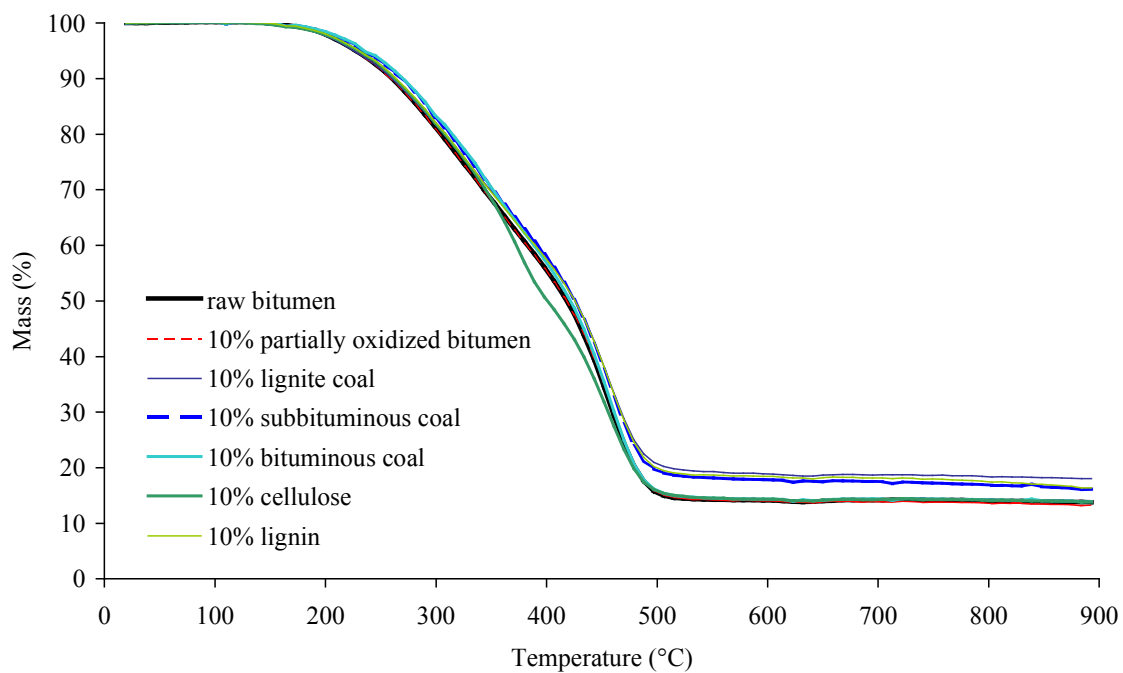


Figure S5. TGA of raw material mixtures with bitumen performed over the range 20-900 °C under N₂ flow rate of 0.33 mL·s⁻¹ and at a heating rate of 0.33 °C·s⁻¹. The TGA of raw bitumen is shown for comparison.