# Suppression of coke formation during bitumen pyrolysis

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## Abstract

Mild pyrolysis (400 °C) of bitumen was investigated to establish ways in which coke formation can be suppressed. Bitumen was diluted to various degrees with solvents that had different hydrogen transfer properties, namely, hydrogen donation, hydrogen shuttling and a solvent with poor hydrogen transfer properties. Additionally the concentration of light products generated during bitumen pyrolysis was manipulated by pressure and batch/semi-batch operation. Coke formation was suppressed by light material, whether added as a solvent, or generated *in situ* during pyrolysis. As anticipated, hydrogen transfer was important, but coke formation was reduced by 35 % at 10 % concentration of even a poor hydrogen transfer solvent. Hydrogen availability and the H:C ratio of the reaction mixture were found to be particularly influential in determining whether coke formed. The results showed that light gases produced during pyrolysis were not irreversible reaction products, but continued to participate in the reaction network to moderate the pyrolysis process and suppress coke formation. Applied to industrial operation, evidence was provided to indicate that liquid yield can be increased and coke formation can be suppressed during visbreaking by co-feeding light gases, typically $C_4$ and lighter hydrocarbons.

Keywords: Thermal cracking, visbreaking, pyrolysis, bitumen, coke, hydrogen transfer

## 1. Introduction

Thermal conversion is the oldest of all refining processes. To this day thermal conversion is industrially employed for the upgrading of heavy oils and bitumens.(1) Conversion takes place through thermal cracking (pyrolysis) of the molecules and the chemistry follows a free radical mechanism. Three main classes of thermal conversion technology are found for bitumen: visbreaking, coking and residue hydroconversion. Visbreaking is a mild pyrolysis process that was originally developed to reduce the viscosity sufficiently for fuel oil applications. Coking is a prolonged pyrolysis process that disproportionates the bitumen into a carbon-rich coke fraction and more hydrogen-rich lighter fractions. Residue hydroprocessing is a process where pyrolysis and hydrotreating are combined to hydrogenate the cracked products as they are produced to increase the quality and yield of liquid products.

The role of thermal upgrading changed over time, as society became more sensitive about the use of carbon. This is especially evident in the changing role of mild pyrolysis as is found in visbreaking, since the emphasis shifted from the production of fuel oil to the increased production of lighter liquid products that have higher value. It is the latter application, namely, the mild pyrolysis of bitumen to increase the yield of lighter liquid products, which is considered in the present work.

In order to increase the yield of lighter liquid products, mild pyrolysis has to be operated at higher conversion. Practically, the maximum conversion is limited by coke formation in the furnace and stability of the atmospheric residue fraction, although there are other constraints too.(2)(3) There is a stoichiometric limit on how much pyrolysis conversion can be performed before carbon rejection by coke has to take place in order to balance the H:C ratio of the feed and products. Coke formation can be suppressed by hydrogen addition, which increases the H:C ratio of the product and decreases the need for carbon rejection. This strategy is employed in residue hydroconversion to obtain an overall increase in H:C ratio of the products, either through direct catalytic hydrogenation with $H_2$, or indirect hydrogenation by hydrogen-transfer from an appropriate hydrogen-donor solvent. The latter approach has extensively been used in direct coal liquefaction.(4) Petroleum refiners did not overlook the analogy and visbreaking combined with hydrogen-donor solvents was investigated,(5)(6) as well as hydrothermal conversion,(7) and ways to generate hydrogen during visbreaking, such as Aquaconversion.(8) Another source of coke formation is free radical addition reactions. Industrially steam is employed to reduce coke formation by increasing turbulence in the flow where feed vaporization is insufficient to do so,(2) and to reduce free radical addition in the vapor phase by dilution. Hydrogen donor solvents can perform a similar function, but with the added ability to terminate free radical reactions through intermolecular hydrogen-transfer.

Bitumen pyrolysis is a well-established, mature and industrially practised conversion process, yet, there are still some opportunities for improvement. In this work we investigated ways to suppress coke formation during the pyrolysis of Canadian oil sands derived bitumen. The investigation probed the science. Model solvents were chosen to differentiate different possible mechanisms of coke suppression and although real bitumen was used, this should not be considered an applied study with direct industrial application. The outcome was unexpected and it generated some new insights into the parameters that are important for suppressing coke formation during visbreaking. Our working hypotheses were:

(a) Lowering the operating temperature will decrease coke formation. There is an inverse relationship between temperature and time required for the same level of cracking conversion in visbreaking.(5) Better liquid selectivity is obtained by operating at lower temperature due to the difference in apparent activation energy for the production of lighter and heavier molecules.(2) This hypothesis was not verified by the present study, but it informed the choice of pyrolysis temperature; all experiments were conducted at 400 °C.

(b) Co-feeding a liquid solvent with bitumen will suppress coke formation. The solvent can reduce free radical addition reactions by dilution and by free radical termination in the case of hydrogen donor solvents. Hydrogen donor solvents are preferred and literature indicates that the hydrogen donor ability of a solvent is crucial to increase liquid yield,(4) and decrease coke formation.(9) This hypothesis was investigated.

(c) Decreasing the production of light gases during bitumen pyrolysis will suppress coke formation. Light gases have higher H:C ratios than liquid products. Consequently, the need to produce coke through hydrogen disproportionation in order to balance the H:C ratio of feed and products will diminish if less light gases are produced. For example, producing pentane ($C_5H_{12}$) as opposed to producing methane ($CH_4$), reduces the stoichiometric coke requirement by 40 %. Over-cracking of lighter liquids at longer residence time was cited as one of the main reasons for increased light gas production.(10) This hypothesis was investigated.

## 2. Experimental

### 2.1 Materials

The experimental investigation was performed with Canadian Cold Lake bitumen, which was supplied through the sample bank of the Center for Oil Sands Innovation (COSI) at the University of Alberta. Two different samples of Cold Lake bitumen were used, one that was aged and one that was fresh (Table 1). These two samples had different coking propensities, as can be seen from the difference in micro carbon residue (MCR) values.

The solvents employed were selected based on their different hydrogen-transfer abilities. The hydrogen donor solvent, tetralin (1,2,3,4-tetrahydronaphthalene) 99 %, was supplied by Sigma Aldrich. Mesitylene (1,3,5-trimethylbenzene) 98 %, also supplied by Sigma Aldrich, was employed as solvent with hydrogen shuttling ability. Naphthalene +99 % supplied by Fischer Scientific, was employed as solvent with poor hydrogen-transfer ability. Praxair supplied nitrogen 99.999 % as compressed cylinder gas.

### 2.2 Equipment and Procedure

All pyrolysis experiments were performed in a semi-batch reactor (Figure 1) that was operated either in batch, or semi-batch mode. The setup was constructed using Swagelok 316 stainless steel tubing and fittings. The reactor was heated by placing it in a heated fluidized sand bath. The temperature inside the reactor was monitored and indirectly controlled by adjusting the temperature of the heated fluidized sand bath. During batch mode operation the reactor was purged and pressurized with nitrogen and then the ball valves V01 and V02 were closed before the reactor was placed in the heated fluidized sand bath. During semi-batch mode operating the same procedure was followed, but ball valve V02 was left open and the pressure inside the reactor was controlled by adjusting the back pressure regulator PCV02.

For a typical experiment the reactor was filled with 5-8 g material (bitumen and solvent), purged and leak tested with nitrogen. If required, the reactor was then pressurized to the desired pressure, before being placed into the preheated fluidized sand bath heater. The heat-up time from room temperature to 400 °C was 5 minutes. The duration of each run was 1 hour, measured from the time heating started. Cooling down at the end of the experiment also took 5 minutes. The reactor was then depressurized. The light gases produced during the reaction and on depressurization was collected in a gas bag and afterwards analyzed. After removing and cleaning the reactor, the reactor and product were weighed to determine the weight of product. The reaction product was removed from the reactor with methylene chloride in a ratio of 1:40. The mixture was stirred for an hour and then the coke was extracted from the diluted pyrolysis product by filtration. The coke fraction was dried and weighed. Material balances for the experiments were typically in the range 97-103 %. All experiments were performed at least in triplicate.

## 2.3 Analyses

The gaseous products were analyzed using an Agilent 7890A gas chromatograph equipped with both flame ionization and thermal conductivity detectors. A Hay Sep R column, 2.44 × 0.003 m (8 ft × ⅛ inch) was employed. The carrier gas used for analysis was helium with a constant flow of 25 $ml \cdot min^{-1}$. The injector temperature was set at 200 °C. The temperature program used started at 70 °C for 7 minutes, then ramping at 10 $°C \cdot min^{-1}$ to 250 °C and holding for 2 minutes, followed by ramping at 30 $°C \cdot min^{-1}$ to 300 °C and holding for 8 minutes.

Viscosity analyses were performed using an Anton Paar RheolabQC viscometer. The RheolabQC was calibrated with a Newtonian viscosity standard specimen whose kinematic viscosity was measured using a capillary viscosimeter of the Ubbelohde type, which was traceable to the national standard of the viscosity. The sample measuring cup used was C-CC17/QC-LTC and on average 4 g of the samples was required for analysis.

A Mettler Toledo ML 3002 balance (3200 g capacity with 0.01 g readability) was used for weighing of reactors, samples and products. Pressurized reactors were weighed before and after reaction, as well as after depressurization. In this way it was possible to also determine the gas yield gravimetrically.

## 3. Results and Discussion

### 3.1 Pyrolysis of diluted bitumen

Three different model solvents were evaluated for their ability to increase the liquid yield from bitumen pyrolysis, namely, tetralin, mesitylene and naphthalene. The solvents were selected based on the difference in their hydrogen-transfer capabilities. It was found that at 4:1 dilution (20 wt% bitumen in solvent), all of the solvents were capable of increasing liquid yield and decreasing coke yield (Table 2). Qualitatively the results were similar to that of a previous asphaltene pyrolysis study at 430 °C, where tetralin, methyl naphthalene and naphthalene were employed as solvents at 3:1 solvent to asphaltene ratio.(11)

As expected, the best results were obtained with tetralin, which is the prototypical hydrogen donor solvent. The liquid yield after 1 hour pyrolysis of neat bitumen at 400 °C was 79.0 ± 2.5 wt%, but for bitumen in tetralin, the liquid yield increased to 87.0 ± 1.0 wt%. The improvement in liquid yield was mainly due to the suppression of coke formation. The coke yield decreased from 7.5 ± 0.2 % for neat bitumen pyrolysis to 2.0 ± 0.8 % for bitumen diluted in tetralin. Although a slight decrease in gas yield was also observed, it was within the experimental error. Tetralin is capable of donating hydrogen (H•) to the free radical species (B•) formed during bitumen pyrolysis (Figure 2a). By transferring a hydrogen atom, which also has an unpaired electron, the free radical is terminated to produce a molecule with paired electrons (H:B). During this process the tetralin is dehydrogenated to 1,2-dihydronaphthalene, which is also a hydrogen donor solvent. The 1,2-dihydronaphthalene can likewise donate hydrogen to free radical species, ultimately being converted into naphthalene. By terminating free radical species, without the solvent being converted into a free radical product (except as intermediate), coking is suppressed.

Possibly the most dramatic demonstration of coke suppression due to an excess of hydrogen donor solvent, was provided by the study of Peng.(12) She demonstrated that the coke yield from asphaltene pyrolysis could be decreased from 38 to 2 wt % by conducing the pyrolysis in the presence of tetralin. The asphaltenes employed in her study was a $C_5$-precipitated asphaltene fraction from Athabasca bitumen. The pyrolysis conditions employed were 430 °C for 1 hour at a tetralin to asphaltene ratio of 3:1. Similar results were reported with the hydrogen donor solvent tetrahydroquinoline.

Although it was anticipated that dilution will play a role in preventing free radical addition reactions, it was surprising that to see that both mesitylene and naphthalene were capable of at least halving the coke yield. Neither of these solvents are hydrogen donor solvents.

Mesitylene is a hydrogen shuttling solvent. It is capable of transferring hydrogen to free radicals formed by bitumen pyrolysis in an analogous way to tetralin, but by doing so, the mesitylene becomes a free radical (Figure 2b). This may help to terminate free radical species capable of forming coke, but the mesitylene must ultimately get the hydrogen back from the bitumen, or itself run the risk of free radical addition. Mesitylene is sterically crowded and self-termination to form mesitylene dimers is difficult and no clear evidence was found that mesitylene dimerization is a meaningful termination pathway. Nevertheless, dimerization was reported for another hydrogen shuttling solvent, methyl naphthalene, during pyrolysis of diluted bitumen at 400 °C and 13.8 MPa $H_2$ pressure.(13) Under such a high hydrogen pressure it is possible to hydrogenate some the naphthalene to tetralin, which is a hydrogen donor solvent. It is also possible to form dimers, because ring-addition is not sterically hindered as in the case of mesitylene. Mesitylene is only a hydrogen shuttling solvent and not a hydrogen donor solvent.

Naphthalene is a poor hydrogen transfer solvent (Figure 2c). The aromatic C–H bonds have high bond dissociation energies, typically of the order of 472 ± 3 $kJ\cdot mol^{-1}$, compared to 375 ± 3 $kJ\cdot mol^{-1}$ for the C–H of a methyl group attached to an aromatic ring as is found in mesitylene.(14) However, aromatic solvents that contain no alkyl groups are not completely inert.(15)(16) The potential participation of naphthalene in free radical propagation by hydrogen abstraction from an aromatic C–H bond depends both on the temperature and the naphthalene concentration. For example, it was reported that the thermal conversion of benzene relative to *n*-hexadecane was 5 times lower when the molar concentration of *n*-hexadecane in benzene was increased from 0.01 to 0.05.(16) Another mechanism that was suggested for naphthalene participation in free radical propagation involves the transfer of hydrogen to one of the carbon atoms in the naphthalene ring to create monohydronaphthalene. This is also called the ipso-mechanism. Some hydrogen exchange was reported for phenanthrene as solvent with coal, but almost no exchange took place with anthracene.(17) In addition, little support was found that the ipso-mechanism was a significant contributor in coal dissolution by 1-methylnaphthalene.(18) Yet, naphthalene was capable of reducing the coke from 7.5 ± 0.2 % for neat bitumen pyrolysis to 3.8 ± 0.5 % for bitumen diluted in naphthalene. Dilution seemed to play a more significant role than hydrogen transfer ability, because naphthalene was effective at reducing the coke yield without being as active for hydrogen transfer as tetralin or mesitylene.

In the pyrolysis experiments (Table 2), the bitumen concentration was 20 %. With so much solvent, it is conceivable that the solvent interfered with free radical addition reactions and in-cage reactions were more easily disrupted. The physical separation (dilution) of free radical species by the solvent was apparently the dominant force for suppressing coke formation, so that even naphthalene, which is not an efficient hydrogen transfer solvent, was effective in reducing the coke yield during pyrolysis compared to neat bitumen.

On a solvent free basis, it was found that disproportionation of hydrogen from liquid phase to gas phase products increased with in increasing hydrogen transfer ability of the solvent.(19) The H:C ratio of gas phase products was the highest with tetralin as solvent (H:C = 3.07) and the lowest with undiluted bitumen (H:C = 2.95). Conversely, the H:C of the liquid phase products was the lowest with tetralin as solvent (H:C = 1.14) and the highest with undiluted bitumen (H:C = 1.37).

The lower H:C ratio of the liquid phase product after pyrolysis of 20% bitumen in tetralin is mainly due to the retention of material in the liquid phase that was rejected as coke during bitumen pyrolysis (Table 2).

### 3.2 Effect of solvent dilution on coke yield

If dilution played an important role in suppressing coke, then the coke yield should be sensitive to the solvent concentration. The participation of poor hydrogen transfer solvents, such as naphthalene, in free radical transfer also decreases in relation to concentration.(15)(16) It was therefore anticipated that a decrease in solvent concentration will lead to a gradual increase in coke yield, but this was not what was observed (Figure 3).

Even with the least amount of solvent evaluated, 10 % naphthalene, the presence of a solvent caused the coke yield during pyrolysis to be decreased from 7.5 % for neat bitumen to around 5 %. This decrease in coke yield was not due the hydrogen transfer ability of the solvent, since naphthalene is a poor hydrogen transfer solvent. A benefit of better hydrogen transfer and hydrogen donation was seen mainly at higher solvent concentrations. At lower solvent concentration, the coke yield was within experimental error similar for all of the solvents.

The effect of solvent concentration of the different solvents on coke yield (Figure 3) indicated that at least four mechanisms were at work to suppress coke formation:

(a) Hydrogen donation was important. Tetralin is a good hydrogen donor solvent and the contribution of hydrogen donation can be seen from the difference in coke yield between tetralin and mesitylene, which is not a hydrogen donor solvent. At a solvent concentration of 50 % and higher there was a meaningful difference at 95 % confidence level based on a two-tailed Student t-test comparison of the means.

(b) Hydrogen shuttling was important. Mesitylene is a good hydrogen shuttling solvent and the contribution of hydrogen shuttling can be seen from the difference in coke yield between mesitylene and naphthalene, which is a poor hydrogen shuttler. The difference was meaningful for a solvent concentration of 20 % and higher at 90 % confidence. Even so, the difference was not meaningful with respect to tetralin.

(c) Dilution was important. The effect of dilution can be seen from the impact of solvent concentration on the coke yield. The coke yield monotonically decreased with an increase in solvent concentration for all solvents over the whole concentration range studied. However, the contribution of dilution is surprisingly small. Even though the average values for coke yield decreased with increasing solvent concentration, the incremental differences between a 1:1 and 4:1 solvent to bitumen were not statistically significant.

(d) Despite its poor hydrogen transfer capability, naphthalene reduced coke yield significantly compared to neat bitumen. Furthermore, naphthalene was able to suppress coke formation significantly even when the solvent to bitumen ratio was 1:10. In addition to those mechanisms already mentioned, there was at least one important mechanism (or more) that was actively suppressing coke formation.

### 3.3 Effect of solvent dilution on pyrolysis

The effect of solvent dilution on pyrolysis extended beyond the impact on coke yield. The liquid yield was also affected by formation of light gases (Table 3).

As the solvent to liquid ratio was decreased, the contribution of free radical stabilisation through hydrogen donor and hydrogen transfer activity diminished. The decrease in liquid yield was expected from the increase in coke yield (Figure 3). The accompanying increase in gas yield with decrease in solvent concentration (Tables 2 and 3) was observed only for bitumen pyrolysis diluted with tetralin and mesitylene; the gas yield for bitumen pyrolysis diluted with naphthalene remained constant. Although the increased gas yield found with tetralin and mesitylene were within the range of experimental error, the increase was monotonic with the decrease in solvent concentration. Conversely, the light gas yield of neat bitumen pyrolysis is the same as that of bitumen pyrolysis in naphthalene, irrespective of the naphthalene concentration. The change seems to be inversely related to change in production of methane (Table 4). The methane exhibited the same trend as the total light gas yield; the methane concentration decreased as the solvent concentration was decreased. The increase in light gas yield at lower solvent concentration was mainly due to an increase in the formation of $C_2$ and heavier hydrocarbons.

It appeared as if at least a portion of the light gases was produced specifically to compensate for the lack of a hydrogen transfer medium. If the reaction mixture has too little material with hydrogen transfer capability, free radical propagation during pyrolysis is not sufficiently moderated. It is not suggested that the pyrolysis mechanism is altered, but rather that the propagation pathway is affected in such a way that more molecules with hydrogen transfer capability are produced until some form of pseudo-equilibrium is reached. Differently put, if the medium has insufficient hydrogen transfer capability, free radical propagation by repeated β-scission will continue uninterrupted, thereby creating more and more light products that will ultimately moderate the reaction (Figure 4). This interpretation is supported by the change in the methane concentration of the light gas (Table 4). Both the light gas yield and the $C_2$ and heavier hydrocarbon concentration of the light gas increased as the hydrogen transfer ability of the medium decreased.

This observation led to the formulation of a different hypothesis about the role and need for light gases during pyrolysis that was different from that outlined in the introduction.

### 3.4 Role of light gases in bitumen pyrolysis

The working hypothesis outlined in the introduction was that any lighter products formed in a closed system will run the risk of over-cracking to produce light gas.(10) It is therefore beneficial to remove the lighter products as soon as they are formed. Based on the reported observations (Table 3), a new hypothesis was formulated. It was postulated that lighter products are beneficial and that removing such products from the reaction system will promote over-cracking to increase the production of light gas and through hydrogen disproportionation increase coke formation.

These two hypotheses differ with respect to what the dominant mechanism is: over-cracking of products due to longer residence time, or over-cracking of products and increased coke formation due to a lack of moderation by hydrogen transfer. The hypotheses are not mutually exclusive, but highlight different aspects of the overall pyrolysis process as being important.

The effect of increasing pressure as means to exploit vapor liquid equilibrium (VLE) to maintain a higher liquid phase concentration of lighter products was studied using a semi-batch reactor. Semi-batch reactor operation resembles a delayed coking process, apart from the fact that all the liquid feed is introduced to the reactor at the same time. The pressure in the reactor was kept constant by a back pressure regulator, which released vapor phase material in excess of what was required to maintain the pressure (Figure 1). For a given pressure the concentration of the lighter products in the liquid phase will remain constant, under the assumptions that the lightest products govern the vapor pressure of the mixture and that the concentration of the lighter products in the vapor phase does not vary much over time. The concentration of naphtha-range products in the gas phase product was minor.

It was found that as the pressure was increased, the coke yield decreased (Figure 5). It supported the previous observations (Figure 3), which indicated that a solvent suppressed coke formation. The light products produced by pyrolysis became the hydrogen transfer solvent. The increase in pressure from 1 to 2 MPa decreased coke yield, the difference being statistically significant at 99% confidence. A further increase in pressure had less of an effect on coke yield, even though coke yield decreased monotonically with an increase in pressure and the change was statistically significant at 90% confidence. This behaviour mimicked that of hydrogen transfer solvents; a little solvent made a big difference, but further suppression of coke formation was only weakly dependent on solvent concentration.

Sachanen pointed out that the influence of pressure depends on the composition of the matrix, which is determined to some extent by pressure through VLE.(5) The main implication is that observed effect of pressure will be sensitive to the matrix, the nature of the VLE and how vapor material is removed from the system. This will be illustrated by examples from literature, which initially seem to be in contradiction to the present results, but are not contradictory when the experimental details are considered.

When bitumen was pyrolyzed in the range 500-530 °C and 100-650 kPa as a thin film, the effect of pressure on coke yield was inconclusive.(20) There was evidence that as the film thickness increased that pressure increased coke yield at ~500 °C, but the same effect was not observed at 530 °C. The vapor phase was diluted by $N_2$ sweep gas flow and light product evolution was not restricted by VLE; the main effect of pressure was on the nature and size of bubble evolution.

The effect of pressure on delayed coking of Athasbasca bitumen was investigated in a pilot plant and it was found that coke yield increased monotonically with an increase in pressure from 0.25 to 1.1 MPa.(21) During this investigation steam was continuously fed to the coker and the hot and cold separator vessels were kept at the same pressure as the coker. The removal of light material was dominated by steam stripping. As the pressure was increased, the removal of lighter products was not decreased, because the rate of removal was determined by the rate of steam stripping. The temperature and duration of the operation were not reported and at high temperature and long residence time, the effect of pressure on coke yield may merely be a reflection of changes in stoichiometry. The increase in coke yield may be due to a different aspect of the operation, namely the increase in water content of the oil phase with increasing pressure. It was reported that coke yield from bitumen pyrolysis at 430 °C for 30 minutes increased in the order: toluene-bitumen mixture < neat bitumen < toluene-water-bitumen mixture.(22) On the other hand, very different behaviour was seen when bitumen was hydrothermally upgraded in such a way that the asphaltenes were extracted into the water-rich phase.(7)

Coke yield is only one aspect of the impact of pressure on selectivity. Another aspect to consider is the yield of light gases. The yield of light gases increased with an increase in pressure (Figure 5). It was not a monotonic increase and it was not clear why the highest gas yield was obtained at 4 MPa, or why the sample standard deviation for the experiments at 4 MPa was much higher than usual. The experiment at 4 MPa was repeated four times. The directional increase in gas yield with increase in pressure supports the hypothesis that an increase in vapor phase residence time leads to over-cracking. In order to confirm the specific contribution of residence time, one can vary the volumetric ratio of the liquid and gas phase, but this avenue of investigation was not pursued.

If Sachanen's(5) view on the impact of pressure on pyrolysis is correct, then it is likely that the outcome of experiments in a closed system (batch) at the same pressure as an open system (semi-batch), would be different.

One set of experiments was performed in batch mode (Figure 5), where the pressure was allowed to develop autogenously. The autogenous pressure reached 2.2 MPa. In a closed system all the light products formed during pyrolysis remain in the reactor and the liquid phase concentration of light products is governed by VLE. As anticipated, the lighter products produced during pyrolysis performed the role of hydrogen transfer solvents and coke formation was lower in the batch reaction than in any of the semi-batch reactions (Figure 5). Surprisingly, the gas yield was not much different from that found during pyrolysis in semi-batch mode at 1 and 2 MPa, even though batch mode represented the longest residence time. The results indicated that the light gas yield was not primarily determined by over-cracking of light products due to a longer residence time at pyrolysis conditions.

The results indicated that even though operating pressure and VLE may play a role, that there is another aspect that influences the yield distribution. The liquid yield obtained from pyrolysis in a closed system was meaningfully higher than the highest liquid yield obtained by semi-batch pyrolysis, which was obtained at 8 MPa (Table 5). The difference was statistically significant at 95 % confidence.

### 3.5 Relationship of viscosity to coke yield

Viscosity is a measure of the resistance of flow. Viscosity may therefore be an indicator of material to be restricted to the local environment, making it more susceptible for in-cage reactions and coke formation. Since the viscosity of bitumen is sensitive to solvent dilution,(23) and coke formation was suppressed even at low solvent dilution (Figure 3), it was speculated that this might be related to the decrease in viscosity.

The viscosity of neat bitumen and bitumen mixed with naphthalene was measured (Figure 6). Although there was a significant difference in the viscosity at low temperature, the difference did not correlate with the change in coke yield. Even when the data was expressed as function of temperature to estimate the viscosity at reaction temperature (not that we suggest such an extrapolation is prudent or accurate), no correlation was found. If the change in viscosity was partly responsible for the change in coke yield, it was not apparent from the viscosity data collected at temperatures below the pyrolysis conditions.

### 3.6 Explaining coke suppression in terms of the Wiehe-model

Wiehe(24) proposed a model that describes coke formation during pyrolysis. It so happened that the model was developed based on the pyrolysis of the vacuum residue fraction of Cold Lake bitumen at 400 °C, which is the heavy fraction of the feed employed in this study. Key elements of the model are:

(a) There is an induction period in pyrolysis during which no coke is formed. The length of the induction period before coke begins to form is related to the solubility of the asphaltenes in the matrix. As long as the asphaltene fraction is solubilized and does not form a separate liquid domain, coke formation is suppressed.

(b) The asphaltene concentration reaches a maximum value at the end of the induction period. The asphaltene concentration starts to decrease once coke starts to form, suggesting a causal relationship between the decrease in the asphaltene content and increase in coke content of the reacting mixture.

(c) Asphaltenes are more reactive than the maltenes and as pyrolysis progresses, the asphaltenes are converted into more carbon rich compounds, also referred to as asphaltene cores. Once these compounds reach the “solubility” limit, separate ordered liquid phase domains (mesophase) are formed, which are dispersed in the continuous liquid phase. The mesophase is deficient in hydrogen. Without sufficient hydrogen to stabilize free radicals conversion continues to produce toluene insoluble material until coke is finally formed.

(d) Not all asphaltenes are equally aggregated in the liquid phase. The asphaltene molecules that are more aggregated tend to form a mesophase more easily. Ultimately all aggregated asphaltenes end up in a mesophase and with prolonged pyrolysis the aggregation number of the asphaltenes remaining in the liquid phase approaches unity. That is, the asphaltenes in the pyrolyzed liquid that did not form coke are unassociated. The asphaltenes also approach a constant H:C ratio and the liquid phase reaches a constant ratio of asphaltenes to non-volatile maltenes.

The size of the mesophase can be manipulated to inhibit coke formation. The asphaltenes can be partly extracted into the water-rich phase during hydrothermal conversion, which effectively prevents an oil-based mesophase from forming.(7) Fine solids can be added to act as adsorption and nucleation sites for asphaltenes to form smaller mesophase domains.(25)(26) Even though fine solids reduced the rate of coke formation, with prolonged pyrolysis the coke yield was not altered,(25) except in the case of native clay that already contained 6 % carbonaceous material.(27) The size of the mesophase domains can also be manipulated by solvent dilution. Smaller mesophase domains (and coke particles) are produced by pyrolysis of more diluted bitumen in solvent mixtures,(26) as well as dilution with solvents having a lower molecular mass.(25) As the concentration of the bitumen in the solvent increases or the molecular mass of the solvent increases, coalescence of mesophase domains increase to produce larger domains (and coke particles). The rate of coke formation is accelerated by the formation of larger mesophase domains, because the area to volume ratio decreases. The smaller transfer area per unit volume effectively restricts the availability of hydrogen that is supplied from the continuous phase to prevent free radical addition reactions. Differently put, the probability of in-cage reactions is increased and thereby the probability of coke formation in the more hydrogen deficient mesophase is increased.

The Wiehe-model for open systems,(24) and the modification of the Wiehe-model for closed systems,(11) employ a maximum solubility limit to describe when asphaltene molecules will form a mesophase.

In order to apply the Wiehe-model to the present results, it should be recognized that there are two opposing forces at work. On the one hand there is the solubility limit of the asphaltenes that can be increased or decreased to suppress or promote coke formation. On the other hand coke formation can be suppressed or promoted by the presence or absence of transferable hydrogen to stabilize the pyrolysis products.

Let us first consider the impact of the solubility limit. Light material and asphaltenes compete for solvency in the bitumen.(28) It was found that coke formation was suppressed with an increase in pressure (Figure 5) and even more so in a closed system, despite the increase in light material. This was contrary to the expectation that the solubility limit would be decreased to promote coke formation. Further verification was obtained by performing the pyrolysis of bitumen in a paraffinic solvent, *n*-decane (Table 6). The coke yield was 3.3 ± 0.9 %, which is not significantly different from 3.7 ± 0.3 % that obtained with mesitylene (Figure 3). The paraffinic nature of the solvent, which should have decreased asphaltene solubility, did not cause an increase in coke yield. The higher light gas yield that was observed was as a result of thermal cracking of the *n*-decane.

One experiment was also performed at conditions that could potentially increase the solubility limit. When aged bitumen was pyrolyzed for 1 h at 400 °C in a mixture with a 90 % mesitylene concentration, the coke yield was 3.3 %. There was no indication of increased suppression of coke formation. It should be noted that a higher mesitylene concentration could potentially also result in an increase in asphaltene aggregation size (increased correlation length),(29) but this does not change the conclusion. Coke yield was not meaningfully affected.

At 20 % solvent concentration, there was little difference in the coke yield obtained with tetralin, mesitylene, naphthalene and *n*-decane as solvents (Figure 3 and Table 6). Coke yield was also a weak function of solvent concentration. It is therefore unlikely that the induction period, which is related to the asphaltene solubility limit, can be used to explain observed the coke yields.

The results in this study pointed to hydrogen availability as the dominating factor in controlling coke yield. In the context of the Wiehe-model, it indicated that both physical and chemical factors played a role in coke suppression. Both the size of the mesophase domains (physical factor), as well as the availability of transferable hydrogen (chemical factor) mattered.

### 3.7 Phase behaviour

Phase behaviour is an important aspect to consider in the description of coke suppression. Phase behaviour was not experimentally investigated and the relative contribution of phase behaviour compared to chemical suppression of coke formation was not determined. Some indication of the phase behaviour at the experimental conditions can nevertheless be obtained from other studies.

The phase behaviour of an Athabasca vacuum residue and *n*-decane mixture up to 350 °C and 3 MPa was reported by Saber and Shaw.(30) At 350 °C there was a concentration region from around 5-45 % bitumen where two liquid phases (L1L2) co-existed at pressures above 1.8-2.2 MPa. The pressure above which an L1L2 region was found increased with temperature. A three liquid phase (L1L2L3) region was found in mixtures of Athabasca vacuum residue and *n*-pentane at around 45 % bitumen at less severe conditions.(31) The additional liquid phases were not identified as mesophases.

Based on the aforementioned literature,(30)(31) it seems likely that the experiments that were conducted at high solvent concentration and high pressure were in a region where more than one liquid phase was present. Based on the results (Figure 3) coking was not promoted by conditions where the probability of multiple liquid phases was highest. It seems that multiple liquid phases affect coking only if one of the phases is a mesophase. The prediction of mesophase formation is more challenging and was not attempted. Mesophase formation depends not only on the composition and operating conditions, but also on the mechanical and thermal history of the bitumen.(32)

### 3.8 Hydrogen availability and implications for industrial operation

Coke formation is the result of hydrogen disproportionation. Hydrogen disproportionation is in turn regulated by local hydrogen availability. The importance of hydrogen donation during pyrolysis to suppress coke formation is undisputed. Hydrogen shuttling and dilution also contributed in their own ways. Yet, the observed coke suppression could not be fully explained just in terms of these three solvent-based effects even in the context of the Wiehe-model. Light material, whether added as a solvent, or generated *in situ* during pyrolysis, affected coke formation in other ways too. Observations from this study and literature are:

(a) The coke yield after prolonged pyrolysis is affected only by the H:C ratio of the feed mixture, since stoichiometry determines the hydrogen disproportionation between different phases. Coke cannot be avoided if there is too little hydrogen. The rate also has an effect. For example, during pyrolysis in the temperature range 430-550 °C the gas phase products are more olefinic (lower H:C ratio) at higher temperature and when the gas phase products are removed, the remaining H:C ratio of the remaining product is indirectly increased, which resulted in coke suppression.(33) For semi-batch systems it indicates that for prolonged operation it is best to operate at higher temperatures and lower pressures, so that the pyrolysis gases can be as olefinic as possible. Increased pressure during coking is detrimental.(21) The beneficial effect of pressure that was observed (Figure 5) is due to the change in the H:C ratio for incomplete pyrolysis. More generally put, an increase in pressure to keep the H:C ratio of the liquid phase as high as possible is beneficial for visbreaking-type of operation, because hydrogen disproportionation is not complete. Pressure is not beneficial for delayed coking-type of operation, because hydrogen disproportionation is driven to completion.

(b) Co-feeding a solvent, or retaining light pyrolysis materials that act as solvents, suppresses coke formation. The solvent modifies the physical properties of the mixture and is effective at concentrations as low as 10 % (Figure 3), the lowest concentration tested in the work. The solvent suppresses coke formation, even when the solvent itself does not have good hydrogen transfer properties. The solvent does not have to be hydrogen-rich to do so. For example, in this study the main solvents employed had lower H:C ratios than bitumen: bitumen (1.4) > mesitylene (1.3) > tetralin (1.2) > naphthalene (0.8).

(c) At high solvent to bitumen ratio, the nature of the solvent determines whether hydrogen donation becomes the dominant mechanism for coke suppression or not. Hydrogen donor solvents can reduce coke formation significantly, by increasing the H:C ratio of the bitumen and decreasing the H:C ratio of the solvent. In order to re-use the solvent in a continuous process, the solvent must be regenerated by hydrogen addition. This is typical of the design of direct liquefaction processes.(4) The beneficial effect of hydrogen donor solvents is well-known.

(d) The most significant finding of the present study was to highlight the role of dissolved light pyrolysis gases as coke suppressants. At the standard pyrolysis conditions evaluated, 400 °C and 1 h, the lowest coke yield and highest liquid yield was obtained by pyrolysis in a closed system (Table 5 and Figure 5). Dissolved light gases contribute to the stabilization of free radicals. This led us to question the commonly held assumption that the production of light gases during pyrolysis is irreversible.

A reaction network that illustrates the action of light materials in coke suppression is shown in Figure 7, which includes the bond dissociation energy (BDE) of the reactions involved.(14) In the reaction network the light material is represented by methane ($CH_4$) and ethane ($C_2H_6$), and a phenyl radical ($\bullet C_5H_6$) represents the aromatic free radicals that are produced by pyrolysis of the bitumen. The reasoning can be explained in the following way. The pyrolysis study by Khorasheh and Gray(16) demonstrated that hydrogen can be transferred from benzene to hexedecane cracking products, despite the higher BDE of aromatic C–H bonds than that of aliphatic C–H bonds. The benzene in their study was present at 95-99 % concentration. It highlighted the importance of reaction probability (concentration), not just probability of reaction (rate constant). Thus, as the concentration of light material is increased, the probability is increased that the light material can be involved in reactions to stabilize free radicals that were formed by pyrolysis. Even though the probability of abstracting hydrogen ($\bullet H$) or methyl ($\bullet CH_3$)

radicals from neutral compounds decreases with increasing BDE, the probability of such an event increases with increasing concentration of the species. Of particular interest is that it is energetically equally demanding to perform hydrogen transfer from toluene as methyl transfer from ethane (Figure 7).

The present work has some practical implications for industrial operation of visbreaking processes. First, it has shown that it is possible to suppress coking during visbreaking by co-feeding light hydrocarbons. The light hydrocarbons can be in the $C_4$ and lighter range. Second, it indicated that there is benefit to conduct visbreaking at higher pressure, because it will increase the concentration of lighter pyrolysis products in the liquid phase to serve the same purpose as an added solvent. Third, it can be inferred from the present work that it is best to operate with the least vapor volume fraction practical. Only light material dissolved in the liquid phase will help to suppress coke formation. The concentrations of light material in the vapor and liquid phases are determined by VLE, which is not directly affected by the volumetric ratio of the phases, but the amount of material in the vapor phase determines how much material is subject to potential over-cracking, with no benefit to the process.

## 4. Conclusions

Coke suppression during mild pyrolysis of oil sands bitumen was studied experimentally. Two approaches were followed. The first was to dilute the bitumen to various degrees with solvents that had different hydrogen transfer properties, namely, hydrogen donation (tetralin), hydrogen shuttling (mesitylene) and a solvent with poor hydrogen transfer properties (naphthalene). The second was to employ pressure and the method of operation (batch versus semi-batch) to manipulate the light product concentration in the undiluted bitumen. Based on the results, the following observations were made:

(a) Hydrogen donation was important, but the contribution of hydrogen donation to suppress coke formation compared to the other solvent effects became meaningful only at a solvent concentration of 50 % and higher.

(b) Hydrogen shuttling was important and the coke yield from the pyrolysis of bitumen in a solvent active for hydrogen shuttling was consistently lower than for a solvent with poor hydrogen transfer ability.

(c) The presence of a solvent was important, with the coke yield being halved at 20 % solvent concentration, irrespective of the hydrogen transfer capabilities of the solvent. In fact, even at 1:10 solvent to bitumen ratio was coke suppression significant. This is likely a physical effect, with transport in the mixture being improved, but the explanation of the effect was not confirmed.

(d) The contribution of increasing dilution to coke suppression was minor, even though coke yield decreased with increase in solvent concentration for all solvents studied.

(e) Lighter products produced during bitumen pyrolysis also served as a solvent and the coke yield could be manipulated through pressure in a semi-batch pyrolysis. Increasing pressure caused more of the lighter products to remain in the liquid phase, which decreased the formation of coke.

(f) The benefits of operating at increased pressure described in (e) is limited to mild and incomplete pyrolysis, as is found in visbreaking processes. An increase in operating pressure is not likely to benefit processes that involve more extensive pyrolysis, as is applied during delayed coking.

(g) The light gas yield was not primarily determined by over-cracking of the light products exposed to pyrolysis conditions for longer. In an open system, where light products could leave the system, the liquid yield remained fairly constant due to a trade-off between coke suppression and over-cracking to increase the light gases. In a closed system this was not the case and the liquid yield increased. It was postulated that this is related to the H:C ratio of the total reacting mixture.

(h) The production of light gases could partly be explained by the need to produce material that is capable of hydrogen transfer to moderate free radical propagation. In the absence of such material, intramolecular free radical propagation by β-scission can continue uninterrupted, since there are insufficient molecules to transfer hydrogen to terminate or transfer the propagation process.

(i) The use of a paraffinic solvent and the increased production of light paraffinic products did not result in increased coke formation. This suggested that the solubility limit in the Wiehe-model, which determines when a separate liquid domain is formed and leads to coke formation, was not an important factor in this study. The results pointed to hydrogen availability as the dominating factor in controlling coke yield. Interpreted in terms of the Wiehe-model, it indicated that the size of the liquid domains and the availability of transferable hydrogen mainly determined the coke yield.

(j) The results indicated that light gas formation during pyrolysis should not be considered as an irreversible reaction product. The light gases continue to participate in the reaction network, likely as hydrogen and methyl transfer agents, to moderate the pyrolysis process and suppress coke formation.

(k) Ways to suppress coke and improve liquid yield during visbreaking were suggested. First, by co-feeding light hydrocarbons (e.g. $C_4$ and lighter) coke formation can be suppressed. Second, it is beneficial to operate mild pyrolysis at higher pressure to increase the concentration of light products in the liquid phase. Third, it is preferable to limit the volume fraction of vapor-space.

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**Table 1.** Characterization of the Cold Lake bitumen used as feed material.

| Description | Aged Cold Lake bitumen | Fresh Cold Lake bitumen |
|---|---|---|
| Micro carbon residue (wt %) [a] | 17.8 ± 0.5 | 15.0 ± 0.7 |
| Asphaltene content (wt %) | 17.6 | 13.4 ± 1.0 |
| Viscosity at 60 °C (mPa·s) | 16200 | 9600 ± 300 |
| Elemental analysis (wt %) | | |
| carbon | 82.6 | |
| hydrogen | 9.5 | |
| nitrogen | 0.7 | |
| sulfur | 4.8 | |
| oxygen (by difference) | 2.4 | |

[a] Determined in accordance of standard test method ASTM D4530.

**Table 2.** Product yields from pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour, without and with dilution in a 4:1 solvent to bitumen mass ratio.[a]

| Feed material | Product yield (wt %) | | | | | |
|---|---|---|---|---|---|---|
| | liquid | | coke | | gas | |
| | x | s | x | s | x | s |
| bitumen | 79.0 | 2.5 | 7.5 | 0.2 | 13.5 | 3.5 |
| tetralin + bitumen | 87.0 | 1.0 | 2.0 | 0.8 | 11.0 | 2.5 |
| mesitylene + bitumen | 85.0 | 1.5 | 3.0 | 0.3 | 12.0 | 3.0 |
| naphthalene + bitumen | 82.7 | 1.3 | 3.8 | 0.5 | 13.5 | 3.0 |

[a] Average (x) and sample standard deviation (s) of three experiments are reported.

**Table 3.** Gas and liquid yields from pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour diluted with different solvent types and at different concentrations.[a]

| Feed material | Solvent to bitumen ratio | Product yield (wt %) | | | |
|---|---|---|---|---|---|
| | | gas | | liquid | |
| | | x | s | x | s |
| bitumen [b] | 0 | 13.5 | 3.5 | 79.0 | 2.5 |
| tetralin + bitumen | 0.25:1 | 12.2 | 2.7 | 83.8 | 1.5 |
| | 1:1 | 11.5 | 3.0 | 86.5 | 2.0 |
| mesitylene + bitumen | 0.25:1 | 13.0 | 2.8 | 83.3 | 2.0 |
| | 1:1 | 12.5 | 2.6 | 84.4 | 2.2 |
| naphthalene + bitumen | 0.25:1 | 13.5 | 2.5 | 82.0 | 1.7 |
| | 1:1 | 13.4 | 2.5 | 82.5 | 1.9 |

[a] Average (x) and sample standard deviation (s) of three experiments are reported.

[b] Repeated from Table 2 for ease of reference.

**Table 4.** Composition of the carbon containing light gas produced during pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour diluted with different solvent types and at different concentrations.[a]

| Feed material | Solvent to bitumen ratio | Composition of the vapor phase product (mol %) [b] | | | | | |
|---|---|---|---|---|---|---|---|
| | | methane | | $C_2$-$C_5$ | | $CO + CO_2$ | |
| | | x | s | x | s | x | s |
| bitumen | 0 | 30 | 4 | 59 | 3 | 10 | 3 |
| tetralin + bitumen | 0.25:1 | 31 | 6 | 55 | 2 | 12 | 1 |
| | 1:1 | 34 | 1 | 51 | 1 | 14 | 1 |
| | 4:1 | 41 | 5 | 31 | 2 | 27 | 5 |
| mesitylene + bitumen | 0.25:1 | 34 | 2 | 53 | 0 | 12 | 1 |
| | 1:1 | 42 | 2 | 47 | 1 | 10 | 1 |
| | 4:1 | 48 | 8 | 33 | 1 | 19 | 1 |
| naphthalene + bitumen | 0.25:1 | 29 | 1 | 57 | 2 | 14 | 2 |
| | 1:1 | 32 | 2 | 61 | 2 | 8 | 1 |
| | 4:1 | 30 | 1 | 55 | 2 | 15 | 1 |

[a] Average (x) and sample standard deviation (s) of three experiments are reported.

[b] A small amount of heavier hydrocarbons was detected.

**Table 5.** Liquid yields obtained after pyrolysis of fresh Cold Lake bitumen at 400 °C for 1½ hours in batch and semi-batch reactors at different pressure conditions.[a]

| Description of experiment | Liquid yield (wt %) | | |
|---|---|---|---|
| | x | s | n |
| Semi-batch, 1 MPa | 91.3 | 0.8 | 3 |
| Semi-batch, 2 MPa | 91.9 | 0.5 | 3 |
| Semi-batch, 4 MPa | 88.4 | 3.2 | 4 |
| Semi-batch, 8 MPa | 92.2 | 1.1 | 3 |
| Batch, autogenous | 94.3 | 0.8 | 4 |

[a] Average (x), sample standard deviation (s), and number of experiments (n) are reported.

**Table 6.** Effect of a paraffinic solvent on the product yields from pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour at a 0.25:1 solvent to bitumen mass ratio.[a]

| Feed material | Product yield (wt %) | | | | | |
|---|---|---|---|---|---|---|
| | liquid | | coke | | gas | |
| | x | s | x | s | x | s |
| *n*-decane + bitumen | 82.4 | 1.0 | 3.3 | 0.9 | 14.3 | 0.3 |

[a] Average (x) and sample standard deviation (s) of three experiments are reported.

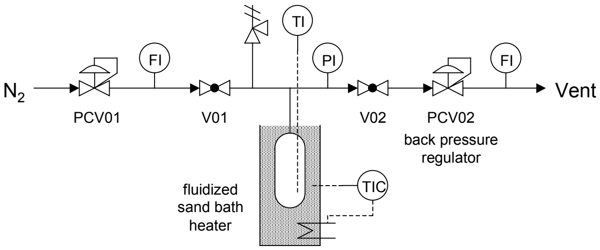

**Figure 1.** Semi-batch reactor employed for pyrolysis of bitumen.

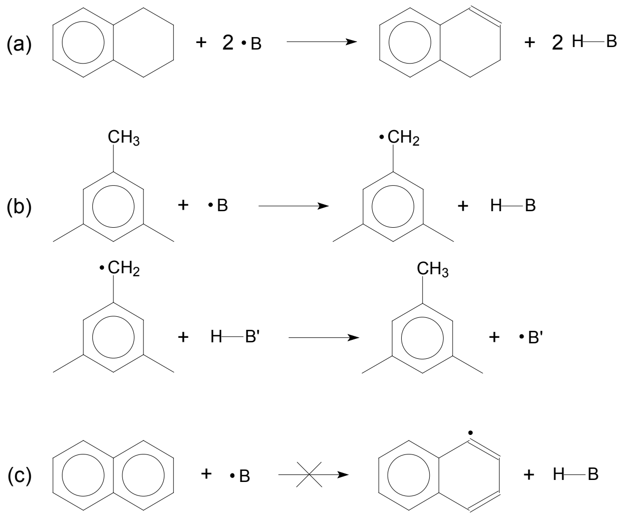

**Figure 2.** Hydrogen transfer action of solvents to bitumen (denoted "B") free radicals: (a) tetralin as hydrogen donor, (b) mesitylene as hydrogen shuttler, (c) naphthalene that is not normally active for hydrogen transfer.

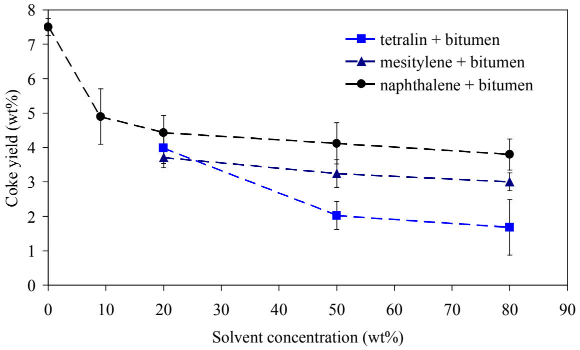

**Figure 3.** Effect of solvent concentration on the coke yield from pyrolysis of aged Cold Lake bitumen at 400 °C for 1 hour.

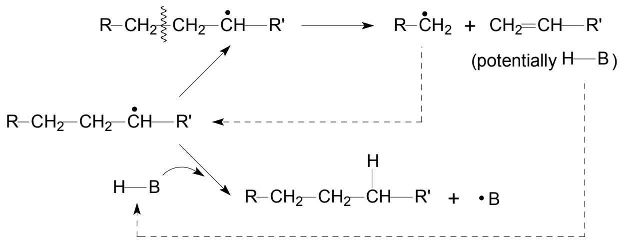

**Figure 4.** Free radical propagation leading to repeated β-scission to produce material that have hydrogen transfer capability and that is able to moderate the reaction of bitumen (denoted "B").

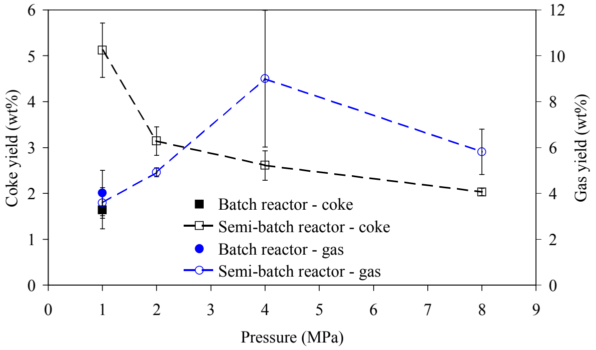

**Figure 5.** Coke yields (batch □, semi-batch ■) and gas yields (batch ○, semi-batch ●) obtained after pyrolysis of fresh Cold Lake bitumen at 400 °C for 1½ hours in batch and semi-batch reactors at different pressure conditions.

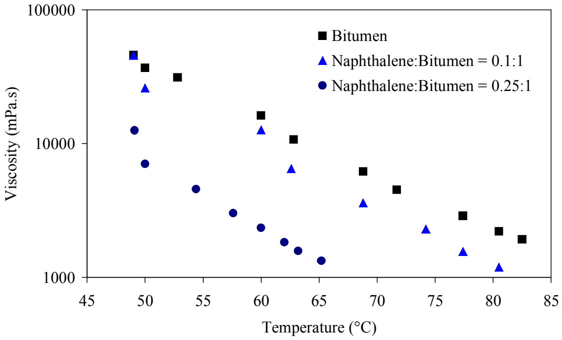

**Figure 6.** Viscosity of neat bitumen (■), and mixtures with 0.1:1 (▲) and 0.25:1 (●) ratios of naphthalene to bitumen.

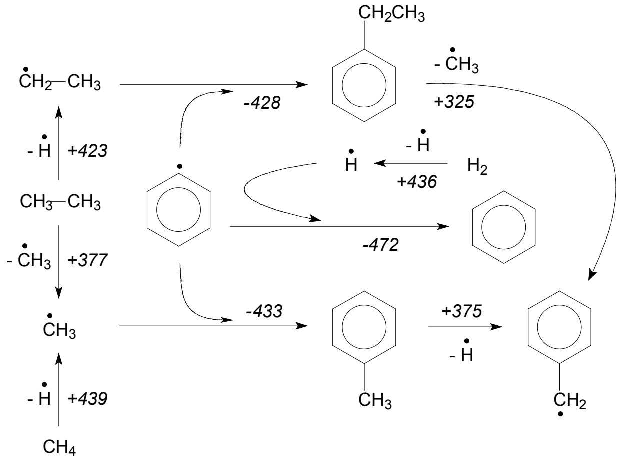

**Figure 7.** Reaction network to illustrate the potential contribution of light gas to suppress coke formation during pyrolysis. The light gases are represented by methane and ethane. Pyrolysed aromatic products are represented by the phenyl radical. Homolytic bond dissociation energies (kJ·mol$^{-1}$) at 25 °C are provided to give an indication of bond strength. Although reactions are represented as mono-directional, all reactions are reversible.