



PROTECTED BUSINESS INFORMATION

FINAL REPORT

INCREASING PIPELINE ACCESS AND REDUCING PROCESSING COST BY ADDRESSING FOULING CAUSED BY OLEFINS/DIOLEFINS IN CRACKED BITUMEN

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EXECUTIVE SUMMARY

Thermally cracked crudes are still not fully accepted for pipeline transportation because they are considered “unstable” in refining operations. When heavy petroleum feedstocks and oil sand bitumen are processed through thermal cracking to reduce viscosity and density to meet pipeline specifications, some undesired unsaturated compounds such as olefins and diolefins are formed that are considered to have the potential to cause fouling and other operational problems in refinery equipment. These types of crudes are currently transported with buffers via pipelines to specific refineries for processing.

There is a lack of quantitative technical information and data in the open literature to show whether all the olefinic compounds in thermally cracked materials are problematic and, if they are, to what extent. Consequently, the basis for the current 1 wt% (measured by H-NMR as *n*-decene equivalent) total olefin content limit in pipeline specification may be questionable. Originally this specification was to be used as a marker for materials that had been thermally cracked and not hydrotreated or hydroprocessed. By imposing a total olefins content limit in cracked crudes as a pipeline specification, the cost of saturating/removing these species has been effectively placed on upstream producers. Therefore, in order to reduce the cost for olefin saturation and removal, it is important to know which (if any) of the specific olefin and diolefin species actually have the potential to cause fouling in refinery operations and, if so, to what extent, or whether there are other sources of fouling within cracked materials and if so, what those sources may be.

In August 2016, Alberta Innovates (AI) approved a research project proposed by CanmetENERGY in Devon under the National Partial Upgrading Program. The project is titled “Increasing Pipeline Access and Reducing Processing Cost by Addressing Fouling Caused by Olefins/Diolefins in Cracked Bitumen”. The scope of this project included a focus on determining fouling tendency, using CanmetENERGY’s Alcor fouling unit, of Western Canadian Select (WCS, benchmark crude from western Canada) spiked with selected olefin and diolefin compounds of different molecular structures at different concentrations. The fouling tendencies of several petroleum fractions acquired from refineries or obtained by distillation of bitumen at our lab, and thermally cracked materials, were also measured.

Research progress reports were submitted to Alberta Innovates (AI) in March 2017 and March 2018. The first report summarized the progress of project activities and research results from project kick-off until February 2017. The second report documented the project progress and achievements from March 2017 to February 2018. The present final project report summarizes the research activities and achievements during the entire two-year period (from October 2016 to December 2018), including those from March 2018 to December 2018 (Phase 3) that have not been formally reported to AI. A presentation on Phase 3 activities and results was given at the CCQTA project meeting on December 6, 2018, following prior discussion with the project steering committee members and with their presence at the meeting.

The overall findings from this project were:

- 1) No evidence was found of significant fouling due to olefins and diolefins.
 - Fouling tendencies of WCS spiked with selected olefin and diolefin compounds were in the low or low-medium fouling range and did not show any apparent effect of the olefin content on fouling tendency (up to 25 wt% measured by H-NMR).
 - The molecular structure, type of olefin, and olefin boiling point did not have significant effects on fouling tendency.
 - Mixtures of olefins and diolefins had fouling tendencies similar to those of individual olefins or diolefins.
 - Several oil fractions (with or without olefins) from refining operations or obtained by distillation of bitumen, and WCS containing olefins from thermally cracked bitumen, had low fouling tendencies.
- 2) When olefins were added to WCS, the main effect was due to diluent addition.
 - Dilution of WCS with *n*-hexane resulted in fouling tendency similar to that of WCS spiked with olefins or diolefins at the same dilution ratio. *n*-Hexane and *n*-hexene had very similar dilution effects.
- 3) Thermally cracked materials showed fouling tendency, although fouling did not correlate with olefin content in WCS.

Project communications among the team members from CanmetENERGY, AI, and project industrial champions as represented by Nexen Energy and Cenovus Energy, as well as the collaborating partner, Canadian Crude Quality Technical Association (CCQTA), have been effective in updating research progress, timely addressing technical and operational issues, and

proposing/modifying new/existing approaches and plans. The progress of the project has been regularly updated through tele-conferences and email communications, and through presentations and discussion at CCQTA project meetings.

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1.0 INTRODUCTION

The extraction and upgrading of oil sands are energy-intensive operations. Several critical challenges have hindered further oil sands development: 1) diluent requirement and limited pipeline capacity; 2) low quality of raw bitumen, reduced value, and limited access to new markets; and 3) high greenhouse gas (GHG) emissions and capital/operating costs for full upgrading. A number of recent studies conducted by Alberta Innovates (AI) have shown that partial upgrading technologies, especially if integrated with upstream operations, can effectively overcome these challenges, and reduce or even eliminate costly diluent use. AI has set a goal of processing 20% of in situ produced bitumen through partial upgrading by 2030, potentially bringing several billion dollars of net economic benefit to Alberta and Canada.^{1,2,3,4}

Of the several partial upgrading technologies being developed at the bench, pilot, and demonstration scales, most are based on thermal cracking (or visbreaking) using different treatments, such as solvent deasphalting, either before or after thermal cracking. It is known that thermal cracking results in the formation of olefins and diolefins. Depending on the severity of residue conversion, the total content of olefins and diolefins in thermally cracked bitumen can vary from below 1 wt% to 3.8 wt% or even higher. Some petroleum refinery operators have the perception that olefins and diolefins present in thermally cracked petroleum or bitumen materials tend to cause fouling problems in refinery heat exchangers and other process equipment. As a result, cracked crudes are still not fully accepted for pipeline transportation due to concerns about their “instability”.

The current pipeline specification for total olefin content in crudes is set at 1 wt% of 1-decene equivalent determined by H-NMR. Olefin content specification was introduced as a marker for thermally cracked material that had not been hydrotreated or hydroprocessed, as olefins formation is correlated to thermal cracking, and olefin content is reduced by hydrotreating or hydroprocessing. By imposing this limit as a pipeline specification, the cost of saturating or removing olefin species is effectively shifted to upstream producers. It is therefore important to determine whether the olefins and diolefins present in thermally cracked petroleum streams or bitumen actually cause significant fouling, or whether this is based on mere supposition, and any increased fouling tendency of cracked materials is due to factors other than the presence of olefins. Unfortunately, the availability of technical information and data on the

fouling propensity of thermally cracked materials containing different olefins and diolefins is very limited in the open literature. Therefore, in order to reduce the potentially high cost required for reducing olefin content in thermally cracked bitumen and to develop partial upgrading technologies that produce fewer olefins and diolefins, it is important to gain a fundamental understanding of the fouling tendencies of crude oils containing olefins and diolefins, as well as the fouling tendencies of thermally cracked materials.

Recognizing the importance of clarifying the “myth” of olefin fouling in thermally cracked bitumen, a number of industry stakeholders along with CanmetENERGY in Devon and Alberta Innovates began informal discussions in the summer of 2015 with the aim of conducting a fundamental study to understand fouling potential associated with olefins and diolefins. The industry participants were Nexen (represented by Nestor Zerpa), Cenovus (represented by Scott Smith), and the Canadian Crude Quality Technical Association (CCQTA) (represented by Andre Lemieux and CCQTA members). It was concluded from these discussions that the study should focus on using model compounds representative of olefins and diolefins that would most likely be formed during thermal cracking, to blend into a heavy crude, to simulate thermally cracked bitumen. A two-page project description was developed by Nestor Zerpa and Scott Smith, which was further reviewed by CanmetENERGY and AI. It was decided to start a joint research project, with CanmetENERGY in Devon leading, AI providing partial funding, and Nexen and Cenovus as industry champions to provide technical advice and consultation.

In the following months, a research proposal was developed by CanmetENERGY in Devon based on the two-page document and follow-up discussions, which was further reviewed and revised by AI, with input from Nestor Zerpa and Scott Smith. After internal and external evaluation, in August 2016, AI approved the project proposal with total funding of \$600K over two years. AI provided 50% of the funding (\$300K) while CanmetENERGY in Devon provided the other \$300K through its federal partial upgrading program under PERD (Program of Energy Research and Development). The project was titled “Increasing Pipeline Access and Reducing Processing Cost by Addressing Fouling Caused by Olefins/Diolefins in Cracked Bitumen”. The scope of the project included a focus on determining the fouling tendencies of crudes (Western Canadian Select, WCS) spiked with selected olefin and diolefin compounds of different molecular structures and at different concentrations. Furthermore, fouling tendencies of thermally cracked materials and several petroleum fractions, acquired from refineries or by

distillation of bitumen at CanmetENERGY in Devon, were also measured. The objectives of the project were (as in the original proposal):

1. Identify the species causing fouling in the thermally cracked bitumen or other petroleum fractions.
2. Identify/establish effective characterization methods for olefin and diolefin species determination and quantification.
3. Provide technical information and experimental data required for revising the current pipeline specification of olefins content.
4. Help in developing post-treatment technologies, other than hydrotreating, to target the removal or saturation of the identified species causing fouling.
5. Help in developing partial upgrading technologies that produce minimal olefins and diolefins.

The ultimate goal was to address the concerns of potential fouling of cracked materials caused by olefins and diolefins in refinery equipment to improve the acceptability of partially upgraded bitumen to pipelines and refiners.

As required by AI, a project steering committee was formed to include the industry champions. The committee members were: Jinwen Chen (CanmetENERGY in Devon), Shunlan Liu (AI), Nestor Zerpa (Nexen), and Scott Smith (Cenovus). Andre Lemieux of CCQTA and Murray Gray of AI joined the steering committee at later dates. The role of the steering committee was to provide research direction and technical guidance to the research team at CanmetENERGY, and to provide additional help and support required to execute the project (such as aid in acquiring feedstocks, and connecting the team with other stakeholders). It was decided to hold project update meetings between the research team and the steering committee every six months in addition to email communications and telephone discussions. It was also decided that the research team at CanmetENERGY in Devon would present the research results once a year at CCQTA project meetings to get advice and input from CCQTA members (Nestor Zerpa representing Nexen and Scott Smith representing Cenovus, both CCQTA members).

The project tasks were discussed and finalized between the research team and the steering committee through various teleconferences, email communications and face-to-face meetings before the project kick-off. Note that the project tasks have been continually revised and updated

over the last three years based on suggestions and feedback received at project update meetings and CCQTA project meetings. These changes and revisions will be given in the individual sections for each phase in this report. The originally proposed tasks were:

Task 0.A: Preliminary fouling tests of Western Canadian Select (WCS) with model olefin/diolefin compounds

Task 0.B: Alcor unit repeatability tests at high and low fouling ranges

Task 1: Systematic fouling tests

1.A. Acquire olefin compounds and feedstocks (new WCS)

1.B. Fouling tests of feedstocks (new WCS)

1.C. Fouling tests of olefins-spiked feedstocks

Task 2: Generation/acquisition of thermally cracked samples

Task 3: Fouling tests of strategically selected cracked samples (cracked bitumen, cracked deasphalted oil (DAO), cracked materials with a boiling point below 343°C)

Task 4: Develop correlations of fouling tendency with oil properties and olefins content

Task 5: Data analysis and results dissemination

This report summarizes the research activities, results, and conclusions in chronological order: Phase 1 covers the time period from October 2016 to February 2017); Phase 2 covers the time period from March 2017 to February 2018; Phase 3 covers the time period from March 2018 to December 2018.

2.0 PROJECT MANAGEMENT AND PROGRESS UPDATES

2.1. PHASE 1 (OCTOBER 2016 TO FEBRUARY 2017)

In May of 2016, CanmetENERGY submitted the final version of the research proposal to AI. Following AI's conditional approval of the proposal in June of 2016, the research team and the steering committee members had a number of email communications followed by a teleconference on July 19, 2016. Participants in this teleconference were:

Jinwen Chen, CanmetENERGY

Mohamed Ali, CanmetENERGY

Teclेमariam Alem, CanmetENERGY

Tingyong Xing, CanmetENERGY

Shunlan Liu, Alberta Innovates

Nestor Zerpa, Nexen Energy

Scott Smith, Cenovus Energy

The purpose of the email communications and tele-conference was to address the comments and requirements of AI in the approval letter. Three conditions set by AI had to be met in order to receive AI funding:

1. Refining the tasks and milestones to the satisfaction of the steering committee;
2. Engaging a US refinery expert in the technical committee;
3. Prepare a plan to describe “how the information generated by the project will be used by the partners to advance the goal of the influencing pipeline specifications, and that if a problem species is identified, what are the potential technologies that can be used to treat the species”.

The above three points were discussed during the tele-conference and through subsequent email communications. It was decided:

1. Given the reduced budget, the priority of the project would be fouling tendency measurements of oils spiked with olefins or diolefins of known concentration and molecular structure. The originally-planned fouling tendency determination of thermally cracked bitumen samples would be performed using only strategically selected samples, depending on the available budget and personnel.
2. The project team would include the Canadian Crude Quality Technical Association (CCQTA) in the technical committee. The CCQTA members come from a number of refining companies and other organizations from Canada and the US. Collectively they would provide valuable input into the research plan and its execution.
3. A plan to disseminate the technical information and data generated from the project was finalized to advance the goal of influencing pipeline specifications and to provide guidelines for treating problematic olefin species that may be identified through the research.

A formal document that addressed the conditions set by AI in the approval letter was prepared and sent to AI on August 17, 2016 (Appendix A). AI formally informed CanmetENERGY on August 19, 2016, that AI’s requests had been completely addressed and the project was ready to start.

A project kick-off meeting via tele-conference was held on October 17, 2016.

Participants in the kick-off meeting were:

Jinwen Chen, CanmetENERGY
Mohamed Ali, CanmetENERGY
Teclemariam Alem, CanmetENERGY
Tingyong Xing, CanmetENERGY
Shunlan Liu, Alberta Innovates
Nestor Zerpa, Nexen Energy
Scott Smith, Cenovus Energy
Andre Lemieux, CCQTA

Project schedule, milestones, and experimental plans were discussed. It was agreed to engage CCQTA members to provide collective feedback through attending and presenting at CCQTA meetings. Participants also discussed the selection of olefin/diolefin model compounds for use in preliminary tests and a plan to present the project background and preliminary results at the CCQTA project meeting on December 14, 2016.

On December 14, 2016, CanmetENERGY presented the project background, tasks, and preliminary results at the CCQTA project meeting held at InnoTech Alberta in Edmonton. The technical committee members of the project, Andre Lemieux of CCQTA, Nestor Zerpa of Nexen, and Scott Smith of Cenovus also attended the meeting. The preliminary results presented at the CCQTA meeting are discussed in this report. Valuable feedback was received from CCQTA members and refinery experts from the United States and Canada.

A follow-up meeting (tele-conference) was held on February 2, 2017, to summarize the feedback and comments received at the December meeting, to update the project progress, and to plan next steps. The following individuals participated in this tele-conference discussion:

Jinwen Chen, CanmetENERGY
Mohamed Ali, CanmetENERGY
Teclemariam Alem, CanmetENERGY
Tingyong Xing, CanmetENERGY
Shunlan Liu, Alberta Innovates
Nestor Zerpa, Nexen Energy

Scott Smith, Cenovus Energy

Andre Lemieux, CCQTA

At this meeting, suggestions received at the CCQTA project meeting were prioritized based on their importance to the scope of the project. It was agreed that fouling tests with WCS spiked with olefins would be conducted at 350°C, which is the maximum temperature in refinery heat exchangers and pre-heaters. It was also suggested that the fouling tests be run for a prolonged time (24 h) to ensure detection of any fouling. Because preliminary tests at 400°C gave replicable results, it was decided to conduct replicate tests at 350°C to establish the baseline for future tests in this project.

The first project progress report was delivered to AI in March 2017. The report summarized project progress and achievements from the proposal submission until February 2017.

2.2 PHASE 2 (MARCH 2017 TO FEBRUARY 2018)

On June 19, 2017, the project team had a tele-conference to discuss the updated project results and review the prepared presentation slides to be presented at the CCQTA meeting on June 21, 2017. The participants in the meeting were:

Jinwen Chen, CanmetENERGY

Mohamed Ali, CanmetENERGY

Teclerariam Alem, CanmetENERGY

Tingyong Xing, CanmetENERGY

Shunlan Liu, Alberta Innovates

Nestor Zerpa, Nexen Energy

Scott Smith, Cenovus Energy

At the meeting, the first set of experimental results on fouling due to model olefin compounds was discussed, along with results of the repeatability tests in the high-fouling range. The project schedule and tasks were discussed and updated based on the shared results. The project progress presentation for the CCQTA meeting on June 21, 2017, was updated based on the comments received at this meeting.

On June 21, 2017, CanmetENERGY presented the project results and progress at the CCQTA meeting held in Calgary. Suggestions and comments were received from CCQTA

members at the meeting, which were recorded and discussed among project team members at a later date in order to revise the project plans and tasks. Some of the comments and suggestions were:

1. Collect gas samples from the reservoir of the Alcor fouling unit for GC analysis to determine the extent of thermal cracking
2. Perform repeatability tests in the low-fouling range (10–20°C)
3. Determine the solids content of WCS-1 and whether it affects fouling tendency
4. Test fouling propensity of processed and/or cracked materials

On November 11, 2017, a project meeting (tele-conference) was held to discuss the latest progress and results and prepare the project presentation for the December 2017 CCQTA meeting. The teleconference participants were:

Jinwen Chen, CanmetENERGY
Mohamed Ali, CanmetENERGY
Teclेमariam Alem, CanmetENERGY
Tingyong Xing, CanmetENERGY
Gonzalo Rocha Aguilera, CanmetENERGY
Shunlan Liu, Alberta Innovates
Nestor Zerpa, Nexen Energy
Scott Smith, Cenovus Energy
Andre Lemieux, CCQTA

Project progress and updated results were discussed. CanmetENERGY shared a draft presentation among the project team members for discussion and feedback. The project team concluded that olefin model compound experiments showed an increase in fouling tendency of WCS-1 but, evidently, olefins were not the only contributors to the fouling behavior of cracked materials. It was decided to test thermally cracked materials and different cuts of thermally cracked materials blended with WCS at different olefin contents. The project team also agreed that CCQTA members would be consulted with regard to revising or establishing a new fouling range (ΔT) based on the project results obtained by November 2017.

CanmetENERGY presented the project results at the CCQTA meeting held at Innotech Alberta in Edmonton on December 14, 2017. Feedback from and discussions among the

participating CCQTA members led to a number of action items to be added into future work of the project. Some of these action items were:

1. The contribution of olefins to fouling was observed, but they were not the only contributors. Some other variables and/or properties, such as P-value and asphaltenes content, should be studied.
2. CCQTA members (Suncor) will provide samples from their refinery process streams to CanmetENERGY in Devon for fouling tests.
3. Tests on blends of thermally cracked materials with WCS showed that blending the light fraction of thermally cracked material with the heavy fraction of WCS did not lead to significant fouling. More tests in this direction should be conducted.
4. Project focus should be directed towards testing bitumen, thermally cracked materials, and various blends.

The second project progress report was delivered to AI in March 2018. The report summarized project progress and achievements from March 2017 until February 2018.

2.3 PHASE 3 (MARCH 2018 TO DECEMBER 2018)

On November 29, 2018, a project meeting (tele-conference) was held to discuss the latest progress and results, and to prepare the project presentation for the December 2018 CCQTA meeting. The participants in the meeting were:

Jinwen Chen, CanmetENERGY
Mohamed Ali, CanmetENERGY
Teclemariam Alem, CanmetENERGY
Tingyong Xing, CanmetENERGY
Gonzalo Rocha Aguilera, CanmetENERGY
Shunlan Liu, Alberta Innovates
Murray Gray, Alberta Innovates
Nestor Zerpa, Nexen Energy
Scott Smith, Cenovus Energy
Andre Lemieux, CCQTA

At the meeting, project progress and results were discussed. CanmetENERGY shared a draft presentation among the project team members for discussion and feedback. Discussions

continued via emails to finalize the presentation for the CCQTA meeting. The project team discussed organizing a workshop to disseminate the project results among stakeholders. CanmetENERGY and AI would organize the workshop and send invitations to stakeholders from industry, pipeline companies, and research institutes.

On December 6, 2018, CanmetENERGY presented the project results and progress at the CCQTA meeting held in Edmonton. CanmetENERGY and AI announced that they were organizing a workshop in January 2019 at which the project results would be presented and different stakeholders were invited to share the results with, and exchange comments and discussion.

3.0 EXPERIMENTAL

There are no standard tests for determining the fouling tendency of petroleum feedstocks. CanmetENERGY has been using the Alcor HLPS unit (Figure 1) to simulate heat exchangers in refinery processes to determine the fouling tendency of petroleum feedstocks and products.

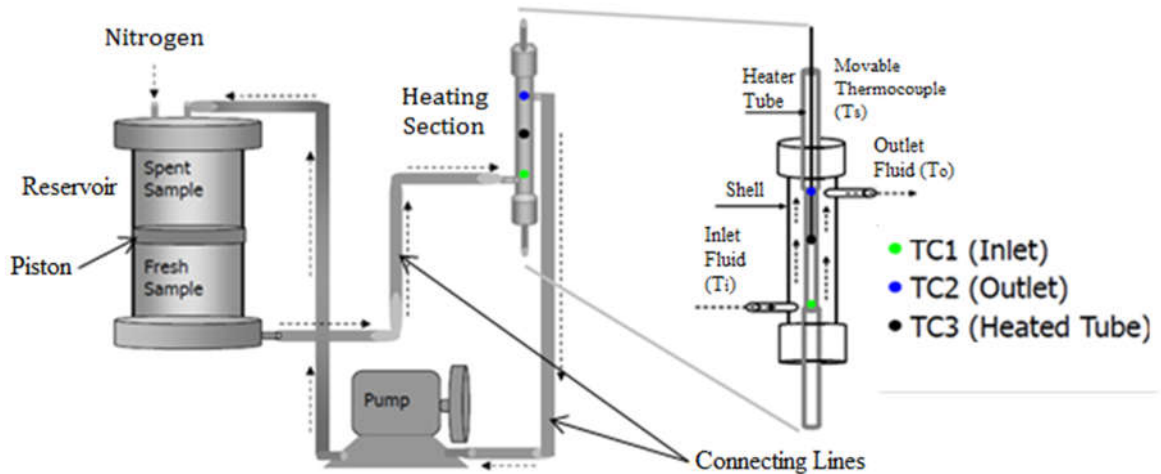


Figure 1 – Schematic of the Alcor HLPS 400 fouling unit

3.1. EXPERIMENTAL PROCEDURE

The Alcor HLPS unit at CanmetENERGY Devon consists of three main components: sample reservoir, circulating pump, and heating section. A schematic diagram of the Alcor unit

and details of the heating section are given in Figure 1. The fouling probe in this unit consists of a heater tube and a shell to simulate a single-pass heat exchanger. The heater tube is made of 1018 carbon steel. The surface temperature at 38 mm into the heating section can be set to different values. Surface temperature is measured using a movable thermocouple that can be placed at different positions along the tube.

The sample reservoir is charged with 500–750 mL of the liquid feedstock. In the single-pass mode, a piston is placed on top of the liquid sample and the reservoir is pressurized with nitrogen to 600 psig. The sample in the reservoir is kept at a constant temperature of 70°C. The sample flows to the heating section at a constant rate of 1 mL/min. The residence time of bulk fluid in the heating section is about 20 s. The sample outlet temperature decrease ΔT (defined as the difference between the outlet temperature at the beginning of the test and at any time during the test) is used as a measure of the degree of fouling: the more fouling, the greater the reduction in the outlet temperature with time. A single-pass run of the Alcor unit takes about 5.25 h and a multiple-pass run takes about 24 h. The experiments and results presented in phase 1 were conducted in single-pass mode at 400°C. The experiments and results presented in phase 2 and 3 were conducted in multiple-pass mode at 350°C. The fouling tendency is categorized into three fouling zones based on the drop in the outlet temperature as follows:

$\Delta T < 15^{\circ}\text{C}$	Low fouling
$15^{\circ}\text{C} \leq \Delta T < 30^{\circ}\text{C}$	Medium fouling
$\Delta T \geq 30^{\circ}\text{C}$	High fouling

4.0 RESULTS AND DISCUSSION-PHASE 1 (OCTOBER 2016 TO FEBRUARY 2017)

4.1. MATERIALS

Fouling tests were conducted using a WCS sample (WCS-0) spiked with model olefin compounds. In addition, replicate tests on thermally cracked bitumen were performed to determine the repeatability and data variation of the Alcor unit. Materials used and testing procedures are described below.

An available WCS sample (WCS-0) was used for conducting the preliminary tests to study the impacts of added model olefins and diolefins on fouling propensity. The olefin and pentane (C5)-insoluble contents, density, and the stability P-value of WCS-0 are given in Table

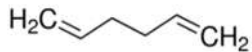
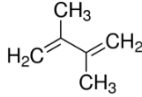
1. A new WCS sample (WCS-1) was obtained from Enbridge, to serve as the feedstock for the systematic tests. WCS-1 properties are reported in the next section of this report.

Table 1 – WCS-0 properties

Property	Value
Density, g/cm ³	0.9213
P-value	2.42
Olefin content, wt% 1-decene equivalent by H-NMR	<0.5
C5-insolubles, wt%	11.43

Three model olefin compounds were identified and used in the preliminary fouling tests. The model compounds were chosen to represent different olefin types: mono-olefin, conjugated diolefin, and non-conjugated diolefin. The three olefin model compounds were selected to have the same carbon number (C6) and similar boiling points. Table 2 shows the model olefin compounds, their type, molecular structures, and boiling points.

Table 2 – Structure, type, and boiling points of model olefin compounds used in preliminary fouling tests

Compound	Structure	Type	Boiling point, °C
1-hexene	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}_2$	Mono-olefin	60
1,5-hexadiene		Non-conjugated diolefin	60
2,3-dimethyl-1,3-butadiene		Conjugated diolefin	65

4.2. FOULING TESTS

Preliminary experiments were conducted to investigate the effects of model olefin compounds on fouling tendency. Samples were prepared by mixing known amounts of the model compounds presented in Table 1 with WCS-0 feedstock at different concentrations. The olefin content of WCS-0 spiked with model olefin compounds was also determined by H-NMR as wt% 1-decene equivalent, which is the method used to determine olefin content for the pipeline specification. Figure 2 shows the olefin concentration determined as 1-decene equivalent compared to the actual concentration of the model compounds (calculated by mixing model compound into the WCS). For mono-olefin (1-hexene) the 1-decene equivalent content was satisfactorily close to the actual concentration. For diolefins 1,5-hexadiene and 2,3-dimethyl-1,3-butadiene, the H-NMR method consistently overestimated the olefin content. This trend was expected as the H-NMR method is based on determining the double bonds in the olefin compounds and estimating the concentration as 1-decene equivalent, which leads to overestimation when two or more double bonds are present in the olefin.

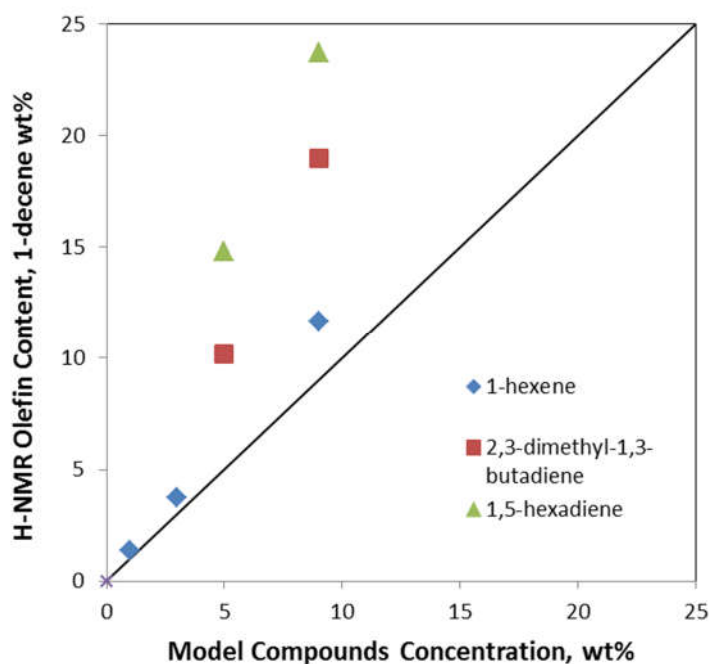


Figure 2 – Olefin content determined by H-NMR as 1-decene equivalent compared to the actual content of the model olefin compounds

WCS-0 samples of different olefin concentrations were prepared with the three model olefins. These samples were tested with the Alcor fouling unit at 400°C in single-pass mode. Results of the fouling tests are shown in Figure 3 along with that of a blank WCS-0 (no model olefin compound added) as a baseline ($\Delta T = 9^\circ\text{C}$). Table 3 also presents the fouling tendency results of these preliminary tests.

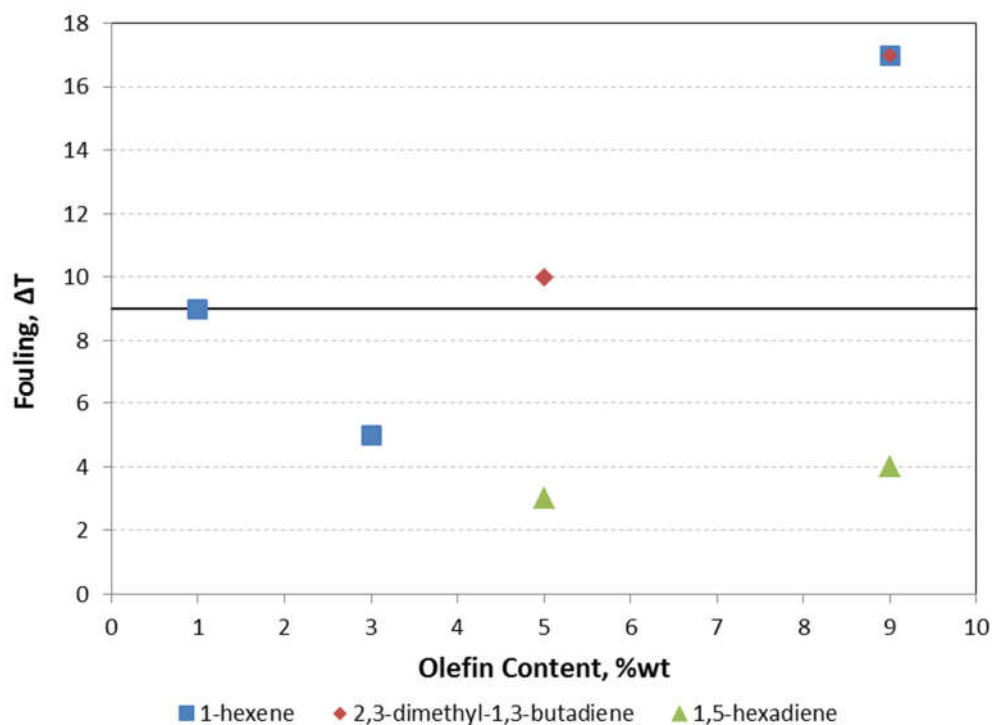


Figure 3 – Fouling tendency of WCS-0 containing different model olefin compounds at different concentrations. The horizontal line indicates the results for the control WCS-0 (no added olefin).

Table 3 – Fouling tendency of WCS-0 containing different model olefin compounds at different concentrations

Sample	Added Olefin Content (wt%)	Total Olefin (wt% as 1-decene by H-NMR)	Fouling $\Delta T(^{\circ}C)$
WCS-0 (blank)	0	<0.5%	9
1 wt% hexene + WCS-0	1	1.4	9
3 wt% hexene + WCS-0	3	3.8	5
9 wt% hexene + WCS-0	9	11.6	17
5 wt% 2,3-dimethyl-1,3-butadiene + WCS-0	5	10.2	10
9 wt% 2,3-dimethyl-1,3-butadiene + WCS-0	9	19.0	17
5 wt% 1,5-hexadiene + WCS-0	5	14.8	3
9 wt% 1,5-hexadiene + WCS-0	9	23.7	4

The difference in fouling tendencies for the 1 wt% and 3 wt% mono-olefin 1-hexene could be due to a combination of variability in the Alcor unit response and experimental error. The fouling tendency at the highest concentration of 1-hexene increased from the low-fouling zone to the medium-fouling zone, indicating that the increased olefin content in the WCS-0 sample changed the fouling tendency.

The conjugated diolefin, 2,3-dimethyl-1,3-butadiene, showed a comparable trend to 1-hexene, as seen in Figure 3 and Table 3. Increasing the concentration of 2,3-dimethyl-1,3-butadiene from 5 wt% to 9 wt% increased the fouling tendency from 10°C to 17°C. This observation is interesting since it has always been considered that conjugated diolefins tend to polymerize and therefore have a stronger impact on fouling, so a higher fouling tendency was expected for the WCS-0 sample containing 2,3-dimethyl-1,3-butadiene. One possible reason that this was not seen is that the temperature of 400°C used in the tests may have been sufficiently high that the 2,3-dimethyl-1,3-butadiene underwent other reactions before polymerization.

The non-conjugated diolefin, 1,5-hexadiene, showed an unexpected response compared to the other two model olefin compounds: concentrations of 5 wt% and 9 wt% resulted in a fouling tendency lower than the fouling tendency of the blank WCS-0. This observation raised a

question regarding the repeatability of the Alcor unit, so a series of experiments were done to determine the reproducibility of fouling measurements (see next section). Regardless, these results with model olefins indicate that different olefin compounds could have different effects on fouling tendency, depending on their type (mono or diolefins) and molecular structure (double bond location and branching). Further investigation of model olefin compounds was done in order to better understand the chemistry and mechanism of fouling caused by different olefin compounds.

4.3. REPEATABILITY OF FOULING TENDENCY TESTS (HIGH FOULING RANGE)

Replicate tests of fouling tendency at 400°C were conducted using a high-fouling material generated in-house by the thermal cracking of bitumen. A total of five tests were conducted. All five samples were collected from the same barrel of thermally cracked material after thorough mixing and homogenization. However, the sample for run 1 was taken, and test run, months before the samples for runs 2 to 5 were taken and run (samples for runs 2 to 5 were taken on the same day).

The fouling tendency results data set was examined for outliers by calculating the first and third quartiles and the interquartile range (IQR) and excluding points higher than 1.5 times the IQR over the third quartile or lower than 1.5 the IQR below the first quartile. The result of run 1 was identified as an outlier and excluded from the calculation of mean and standard deviation. We speculate that this difference in fouling tendency was due to the significant time lag between conducting runs 2 to 5 as compared to run 1, which indicates a potential effect of storage time on thermally cracked material characteristics. The included data showed good repeatability with a mean value of $76.3 \pm 1.3^\circ\text{C}$. Table 4 and Figure 4 show the results from the replicate tests and their mean and standard deviation. Another set of repeatability tests were conducted to test the variation of data in the lower fouling range using WCS-1 that was used in the tests of this project. Results of low fouling range repeatability are presented in Section 5.2.

Table 4 – Results of replicate fouling tests with calculated mean and standard deviation

Run	Fouling, ΔT ($^{\circ}\text{C}$)	Remarks
Run 1	53	Outlier, excluded
Run 2	77	
Run 3	75	
Run 4	78	
Run 5	75	
Mean	76.3	
Standard deviation	1.3	

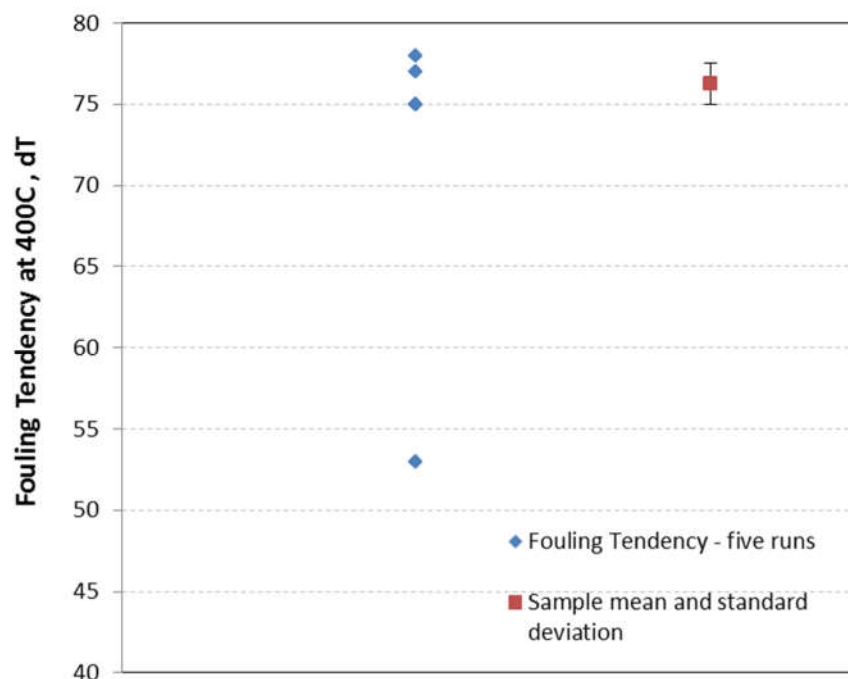


Figure 4 – Graphical representation of the replicate tests and their mean and standard deviation (SD) as error bars. The value at 53 $^{\circ}\text{C}$ was discarded from the calculation of the mean and SD as an outlier.

4.4. CONCLUSIONS OF PHASE 1

1. Three olefin model compounds were tested at different concentrations in WCS-0: 1-hexene, 2,3-dimethyl-1,3-butadiene, and 1,5-hexadiene; 1-hexene and 2,3-dimethyl-1,3-butadiene showed a similar trend of increasing fouling tendency with increasing olefin concentration. However, even at an olefin content of 9 wt%, the fouling tendency of the samples containing 1-hexene and 2,3-dimethyl-1,3-butadiene was just over the limit of

the low-fouling zone. The fouling tendency of 1,5-hexadiene was consistently below that of blank WCS-0 (considered to be within measurement uncertainty), and did not change with increasing concentration.

2. Tests with a known high-fouling material were conducted to determine the variability of the fouling propensity analysis. Five replicate tests were conducted. The replicate tests resulted in a mean fouling value of 76.3°C with a standard deviation of 1.3°C.

5.0 RESULTS AND DISCUSSION-PHASE 2 (MARCH 2017 TO FEBRUARY 2018)

5.1 MATERIALS

In this second set of tests of the fouling tendency of model olefin compounds, CanmetENERGY used WCS-1 as the feedstock to be spiked with model olefin compounds. The properties of the WCS-1 sample are presented in Table 5, which shows that WCS-1 has very low olefin and solids contents. Figure 5 shows the simulated distillation profile of WCS-1.

Table 5 – The properties of WCS-1 feedstock

Tests	Value
Density, 15.6°C, g/cm ³	0.9326
P-value	2.4
Olefin content, wt% 1-decene equivalent by H-NMR	<0.5
C5 insoluble, wt%	12.1
Solids content, wt%	<0.01

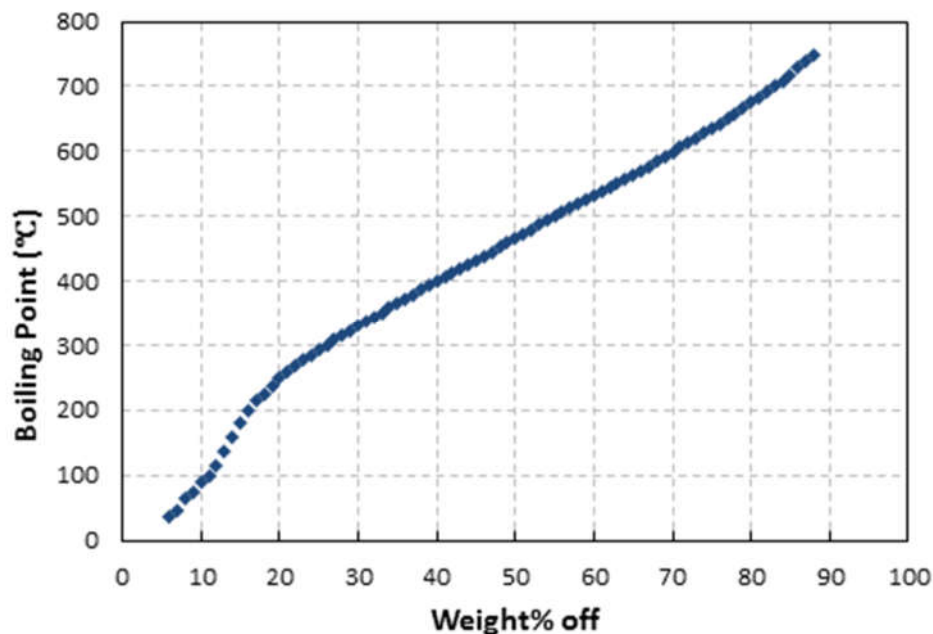


Figure 5 – Simulated distillation profile of WCS-1

In this second project phase, in addition to 1-hexene, which was used in the first project phase, two new model olefin compounds were chosen for these fouling tests. The selection of these two model compounds, 2-methyl-2-pentene and trans-2-pentene, was based on the data on olefin compounds in thermally cracked bitumen reported by InnoTech Alberta. It is expected that these two olefin compounds would be among the most abundant olefins generated during thermal cracking of bitumen. Table 6 shows the model olefin compounds, their molecular structures, and boiling points.

Fouling tests were also conducted for a blend of a thermally cracked stream with WCS-1. The thermally cracked stream was the IBP (initial boiling point) to 280°C fraction distilled from a thermally cracked bitumen. Properties of the IBP–280°C fraction are presented in Table 7. The preparation procedure for the test sample is given in Figure 6. First, both the thermally cracked bitumen and WCS-1 were distilled into 280°C+ fractions and 280°C– fractions. The 280°C– fraction with 6.2 wt% 1-decene equivalent of olefins from the thermally cracked bitumen was then blended with the 280°C+ fraction from WCS-1 in the appropriate proportions according to the simulated distillation (SimDis) data of WCS-1 to form the blend, which is called Product A.

Table 6 – Molecular structures and boiling points of model olefin compounds used in the second phase of the project

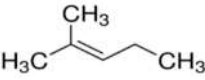
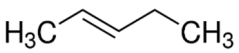
Compound	Structure	Boiling point, °C
1-hexene	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}_2$	60
2-methyl-2-pentene		38
Trans-2-pentene		37

Table 7 – Properties of the IBP–280°C fraction from thermally cracked bitumen

Tests	Value
Density, 15.6°C, g/cm ³	0.8505
Olefin content, wt% 1-decene equivalent by H-NMR	6.2
Diene value, g I ₂ /100g	2.1
C5 insoluble, wt%	0

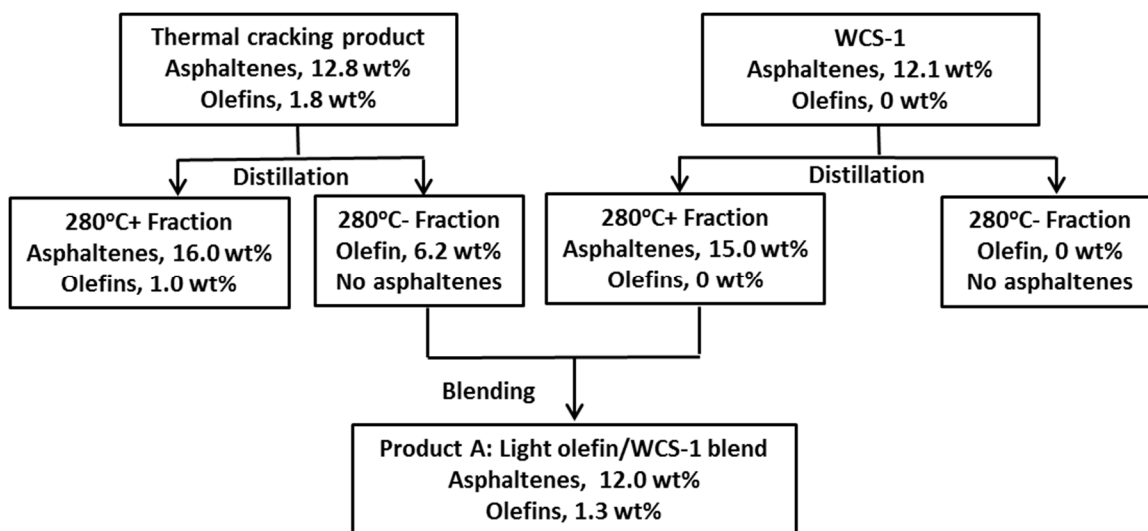


Figure 6 – Preparation procedure for the blended sample with thermally cracked stream and WCS-1

5.2. REPEATABILITY OF FOULING TENDENCY TESTS (LOW FOULING RANGE)

In the first phase of the project, tests were conducted at 400°C for 4 h to determine the repeatability of tests of fouling tendency in the high-fouling range, by using a high-fouling thermally-cracked material generated in-house at the CanmetENERGY Devon lab. Since most of the fouling tendency results of WCS-1 spiked with olefin model compounds were in the low-fouling range, it was decided to establish the repeatability of the fouling unit in a range closer to the range of results of the model olefin compounds experiments. The repeatability tests of fouling tendency in a lower fouling range than the first repeatability test were conducted at 350°C for 24 h. The test material was prepared by blending WCS-1 with 20 wt% of thermally cracked bitumen generated in-house. A total of four runs were conducted and the mean and standard deviation of the results were calculated. The data show good repeatability, with a mean value of 22.8±2.7°C. Table 8 and Figure 7 show the fouling results for both the high- and low-fouling-range replicate tests plus the means and the standard deviations.

Table 8 – Results of replicate fouling tests in the high and medium fouling ranges with calculated means and standard deviations (outlier removed from the high-fouling range data)

Run	Fouling, ΔT ($^{\circ}\text{C}$), high-fouling range	Fouling, ΔT ($^{\circ}\text{C}$) medium-fouling range
Run 1	77	20
Run 2	75	23
Run 3	75	21
Run 4	78	27
Mean	76.3	22.8
Standard deviation	1.3	2.7

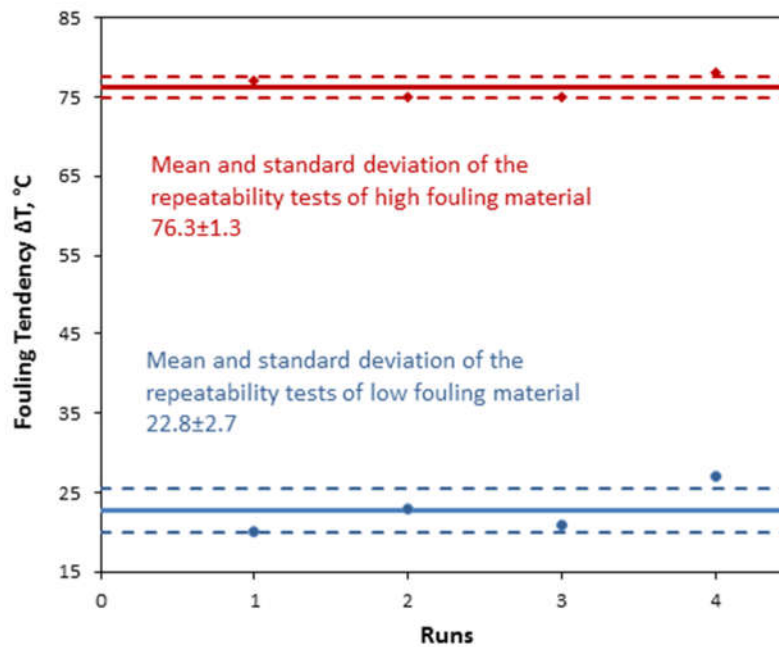


Figure 7 – Graphic representation of the replicate tests; means and standard deviations shown as broken lines

5.3. MODEL OLEFIN COMPOUNDS AND REAL OLEFIN SAMPLE BLENDED WITH WCS-1

After discussions at the CCQTA meeting in December 2016, it was decided to conduct all the remaining fouling tests for this project at 350°C for 24 h to avoid potential thermal cracking of the test materials. Another set of experiments were conducted to investigate the effect of model olefin compounds on fouling tendency. The test samples were prepared by mixing 9 wt% of the model olefin compounds presented in Table 6 with WCS-1 feedstock (the mixing was done separately with each of the three model olefin compounds). The olefin contents of the three prepared samples were also determined by H-NMR as wt% 1-decene equivalent, as shown in Table 9.

Table 9 – Fouling tendency of WCS-1 blended with thermally cracked stream and different model olefin compounds

Samples	Density, 15.6°C (g/cm ³)	Added olefin content (wt%)	Total olefin (wt% as 1-decene by H-NMR)	Fouling ΔT(°C)	P-value
WCS-1 (blank)	0.9326	0	<0.5%	1	2.4
9 wt% 1-hexene + WCS-1	0.9044	9	11.3	17	2.1
9 wt% 2-methyl-2-pentene+ WCS-1	0.9111	9	4.5	19	2.1
9 wt% trans-2-pentene + WCS-1	0.9098	9	7.3	14	2.3
Product A	0.9636	0	1.3	10	2.6

To obtain the baseline, the fouling tendency of a WCS-1 blank sample was also investigated at 350°C for 24 h. The fouling tendency of WCS-1 was 1°C, which indicates that WCS-1 is a very stable crude oil with a very low fouling tendency.

The test results of WCS-1 spiked with model olefin compounds are summarized in Table 9. It can be seen that the fouling tendencies of the three blended samples were similar, and were in the low- to low-end of medium fouling ranges even for olefin content as high as 9 wt%.

The properties and fouling tendency results for Product A are also presented in Table 9. It can be seen that the density of Product A is higher than those of the other three blended samples containing model olefin compounds due to the addition of the 280°C– fraction obtained from thermally cracked bitumen. This observation is also evident from the SimDis data shown in Figure 8. The total olefin content of Product A was 1.3 wt% 1-decene equivalent. The fouling tendency of Product A was 10°C, which also lies within the low fouling range.

The fouling tendency results for the three samples containing model olefin compounds and Product A showed that they all had low to low-medium fouling tendency, although their fouling tendencies were consistently higher than that of blank WCS-1. The differences in fouling tendencies were due to the contributions by the olefin compounds. However, the observed fouling tendencies of these samples were also consistently much lower than that of the total liquid product from thermal cracking of bitumen (~76°C as shown in Table 8). This observation suggests that olefin compounds were not the only contributors to the fouling, and other properties and characteristics, such as asphaltene content and stability P-value, might also contribute to the observed fouling of cracked materials.

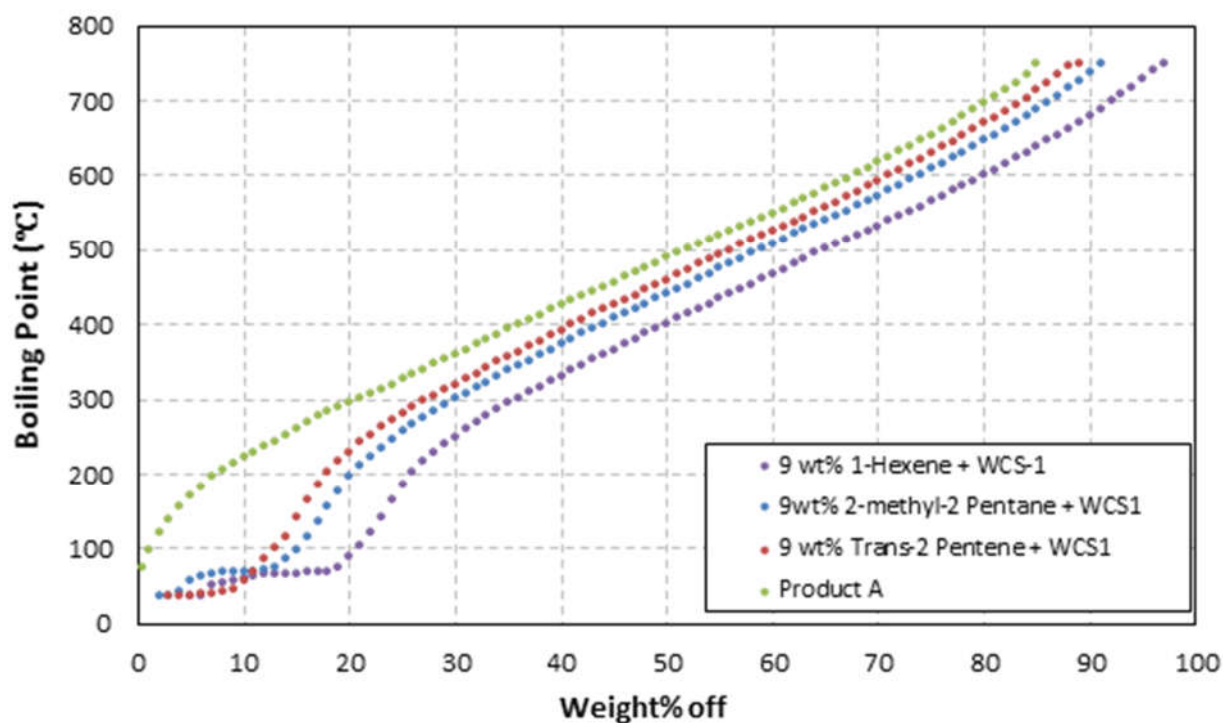


Figure 8 – Simulated distillation profiles of test samples

To determine the extent of thermal cracking during the fouling tests, the gas mixture in the headspace of the reservoir of the Alcor unit was collected and analyzed by gas chromatography (GC). The GC analysis was normalized after correction for nitrogen content. No gas discharge was allowed during the fouling tests in order to collect all hydrocarbon gases generated. The gas analysis results are presented in Table 10. It was observed that the total yields of hydrocarbon gases from the fouling tests with 9 wt% 2-methyl-2-pentene in WCS-1 and 9 wt% trans-2-pentene in WCS-1 were 0.19 and 0.26 g per 100 g feed, respectively, which indicates that the extent of thermal cracking is insignificant during the fouling tests. The yield of hydrocarbon gas from Product A was 0.01 g per 100 g feed, which indicates there was even less thermal cracking during the fouling test of Product A.

Table 10 – Hydrocarbon gas yield from fouling tests. ND means not detected.

	9 wt%-2 methyl-2-pentene +WCS-1	9 wt%-trans-2-pentene +WCS-1	Product A
Hydrocarbon gas	Yield (g gas/ 100 g feed)	Yield (g gas/ 100 g feed)	Yield (g gas/ 100 g feed)
<i>n</i> -propane	0.00	0.00	ND
<i>iso</i> -butane	0.01	0.01	ND
<i>n</i> -butane	0.05	0.06	ND
<i>iso</i> -pentane	0.04	0.04	0.00
<i>n</i> -pentane	0.03	0.03	0.00
<i>trans</i> -2-pentene	ND	0.09	ND
2-methyl-2-butene	ND	ND	0.00
Hexanes	0.06	0.02	0.01
Heptanes	0.00	0.00	0.00
Total	0.19	0.25	0.01

5.4. CONCLUSIONS OF PHASE 2

Repeatability tests of the fouling unit were conducted on a low-fouling material prepared by blending WCS-1 with 20 wt% thermally cracked bitumen. Fouling tests were conducted using WCS-1 spiked with three model olefin compounds as well as a blend of the 280°C– fraction from thermally cracked bitumen and the 280°C+ fraction of WCS-1. The experiments and results led to the following conclusions:

1. Replicate fouling tests of lower-fouling material were conducted at 350°C for 24 h to determine the variability of Alcor unit results in this range. Four replicate tests were conducted. The replicate tests resulted in a mean fouling value of 22.8°C with a standard deviation of 3.1°C.
2. Three olefin model compounds (1-hexene, 2-methyl-2-pentene, and trans-2-pentene) were used to obtain three samples containing 9 wt% olefin concentration in WCS-1. The fouling tendencies of WCS-1 spiked with these three olefin compounds were within the same range, just around the limit of the low-fouling zone. The results showed that, even at such a high concentration of olefins, the fouling tendency was still low, which suggests that olefins were not the sole contributors to fouling in thermally cracked materials. Other properties, such as asphaltene content and stability P-value, might also have contributed to the observed fouling of cracked materials. Analysis of the hydrocarbon gases collected from the sample reservoir of the Alcor unit confirmed that thermal cracking at the test conditions was insignificant.
3. The fouling tendency of the 280°C+ fraction of WCS-1 blended with the 280°C– fraction of thermally cracked bitumen was 10°C. This indicates that the light olefins present in the 280°C– fraction of the thermally cracked bitumen did not cause significant fouling. Therefore, the high fouling observed with the fully thermally cracked bitumen (Table 8) was caused, not only by these light olefins, but by other factors as well, that may include properties such as olefins of high molecular weight, asphaltene content, and stability of the material.

6.0 RESULTS AND DISCUSSION PHASE 3 (MARCH 2018 TO DECEMBER 2018)

6.1. MATERIALS

6.1.1. MODEL OLEFIN COMPOUNDS AND MIXTURES

In these tests of fouling tendency of model olefin compounds, WCS-1 was used as the feedstock to be spiked with model olefin compounds. The properties are presented in Table 5. It shows that WCS-1 has very low olefin and solids contents. Figure 5 shows the simulated distillation profile of WCS-1.

In the third project phase, in addition to 1-hexene, 2-methyl-2-pentene, and trans-2-pentene, which were used in the second phase, two new model olefin compounds with different boiling points were chosen to test fouling tendency. Furthermore, the effect of mixing different olefins was conducted with these olefin compounds. Two mixtures were tested: Mixture 1: 2-methyl-2-pentene; 2,3-dimethyl-1,3-butadiene; 1,7-octadiene (3 wt % each); and Mixture 2: 2-methyl-2-pentene; 2,3-dimethyl-1,3-butadiene; 1,7-octadiene; trans-2-pentene; hexene; octene (1.5 wt% each). The effect of dilution on fouling tendency was also tested by using 1-hexane at 9 wt% in WCS-1. Table 11 shows the model olefin compounds, their molecular structures, and boiling points.

Table 11 – Molecular structures and boiling points of model olefin and paraffin compounds used in the second phase of the project

Compound	Structure	Boiling point, °C
Trans-2-pentene		37
1-hexene	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}_2$	60
1-hexane		68
2,3-dimethyl-1,3-butadiene		65
2-methyl-2-pentene		67
1,7-octadiene		118-120
1-octene		122

6.1.2. DIFFERENT PETROLEUM PRODUCTS (GENERATED IN-HOUSE OR OBTAINED FROM REFINERIES)

Coker gas oil and vacuum gas oil (VGO) were received from a CCQTA member and HVGO and LGO were obtained in-house from bitumen. These samples were run at 350°C for 24 h for the fouling tendency test.

6.2. MODEL OLEFIN COMPOUNDS AND OLEFIN COMPOUND MIXTURES BLENDED WITH WCS-1

As was shown in Phase 2 of this study, WCS-1 is a very stable crude oil with very low fouling tendency. The test results of WCS-1 spiked with model olefin compounds and mixtures are summarized in Table 13.

Table 12 – Fouling tendency of WCS-1 blended with different model olefin compounds and olefin mixtures

	Samples	Fouling ΔT (°C) 24 h @ 350°C	Olefin boiling point (°C)	Added olefin content (wt%)	Olefin content by NMR (wt% 1-decene)	P-value
1	WCS-1 (blank)	1	---	0	0	2.42
2	9 wt% hexene+WCS-1	17	63	9.0	11.3	2.14
3	9 wt% hexane+WCS-1- dilution effect	17	68	0	0	2.09
4	9 wt% trans-2- pentene+WCS-1	14	37	9.0	7.3	2.29
5	9 wt% 2-methyl-2- pentene+WCS-1	19	67	9.0	4.5	2.17
6	9 wt% 1,7- octadiene+WCS-1	17	118-120	9.0	25.3	2.02
7	9 wt% 1- octene+WCS-1	6	122	9.0	12.2	2.10
8	9 wt% olefin mixture 1+WCS-1	7		9.0	16.2	2.22
9	9 wt% olefin mixture 2+WCS-1	8		9.0	13.4	2.14

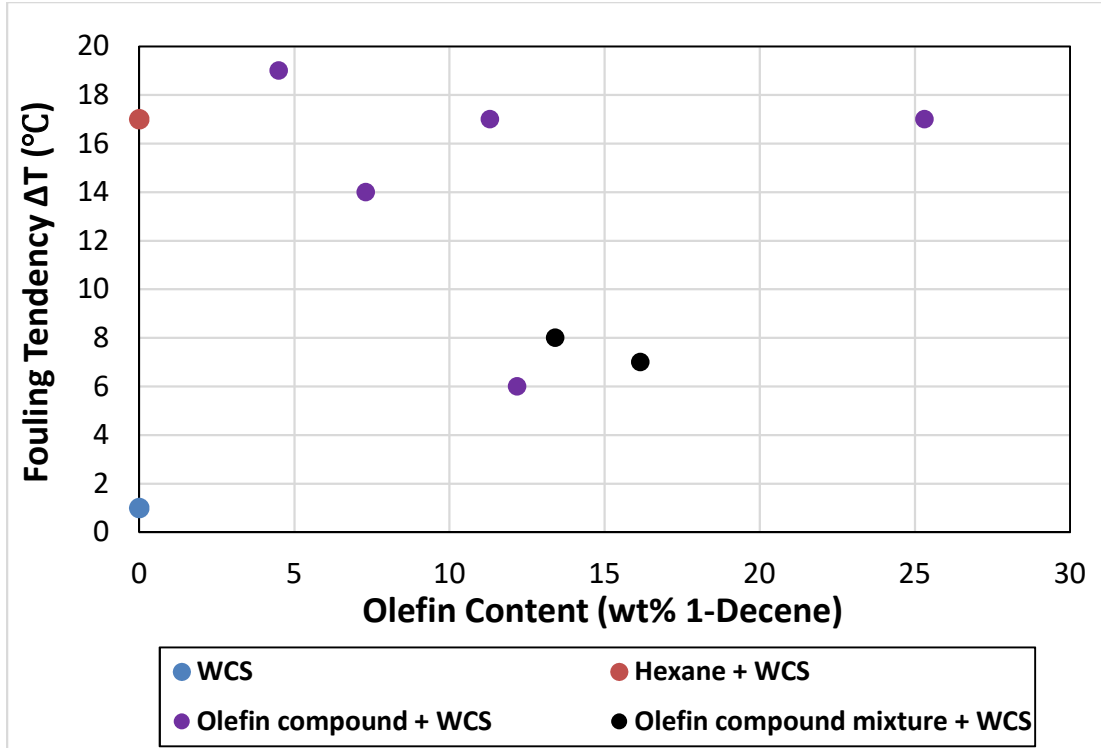


Figure 9 – Fouling tendency of blends with different olefin contents

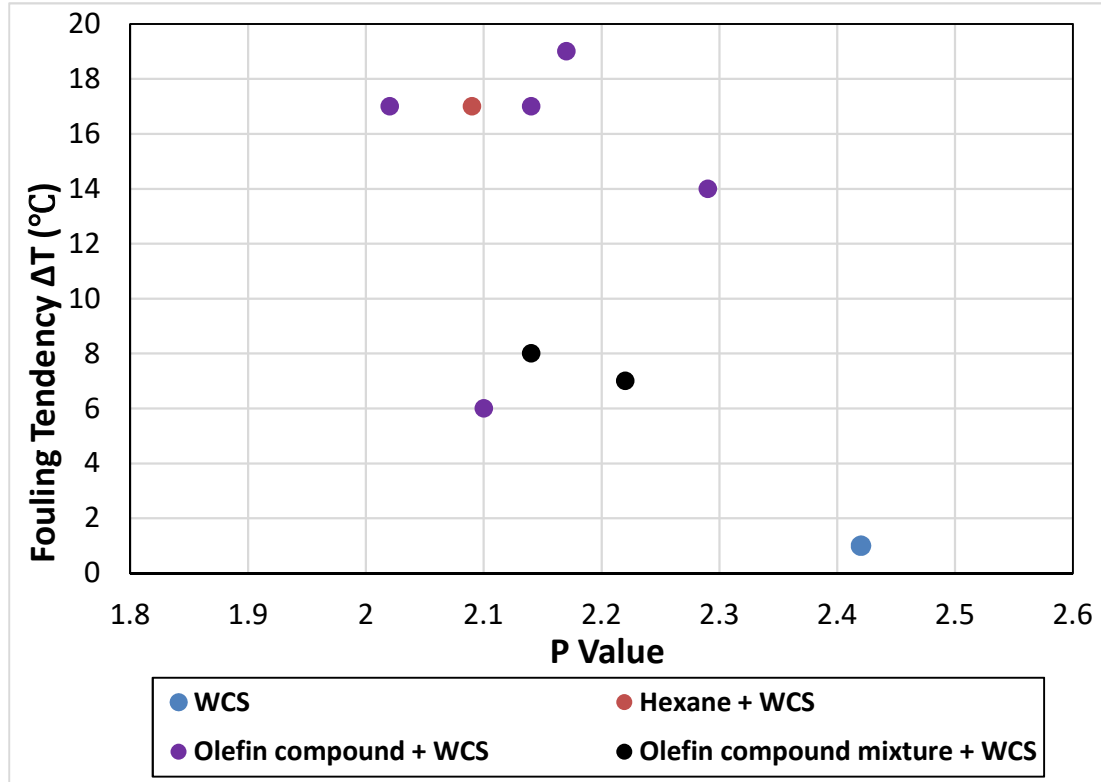


Figure 10 – Fouling tendency of blends with different P-values

Figure 10 shows the effect of olefin content on the fouling tendency of the blended samples. The results showed that fouling tendencies were in the low- to low-medium fouling range and olefin content had no apparent effect on fouling tendency. Structure and type of olefin and mixing of different olefins had no significant effect on fouling tendency. The effect of P-value on the fouling tendency of the blended samples is presented in Figure 11. The results show that the addition of olefins and paraffin resulted in a slight decrease in P-value compared to raw WCS, although they were still in the stable zone. P-value did not show a significant effect on fouling tendency. Furthermore, WCS spiked with *n*-hexane showed a fouling tendency similar to that of WCS spiked with olefin compounds.

6.3. FOULING TENDENCY OF DIFFERENT PETROLEUM PRODUCTS

Results for refinery products are presented in Table 13. The fouling tendency of all products falls in the low range despite olefin contents up to 3.4 wt% (as 1-decene). Compatibility tests show that all of them are also solvent oils (values of solubility blending number of solvent oil (SSO) are shown in the table). This observation further suggests that olefin compounds are not the only contributors to the fouling and that lighter fractions do not contribute to the fouling tendency in isolation. This observation does not exclude the possibility that light fractions could contribute to an increase in fouling tendency when combined with other oil components.

Table 13 – Fouling tendency of refinery products

Feedstock of thermal cracking	Fouling $\Delta T(^{\circ}\text{C})$ 24 h@350 $^{\circ}\text{C}$	Olefin content tested by NMR (wt% 1-decene)	Compatibility test
			Solvent oil, SSO
HVGO from bitumen	11	0	57.6
LGO from bitumen	2	0	46.3
Refinery VGO	10	0.5	35.9
Refinery coker gas oil	10	3.4	51.4

ΔT was graphed against time for some of the refinery products. The data in Figure 11 show that the fouling, represented as ΔT , steadily increases over the test time.

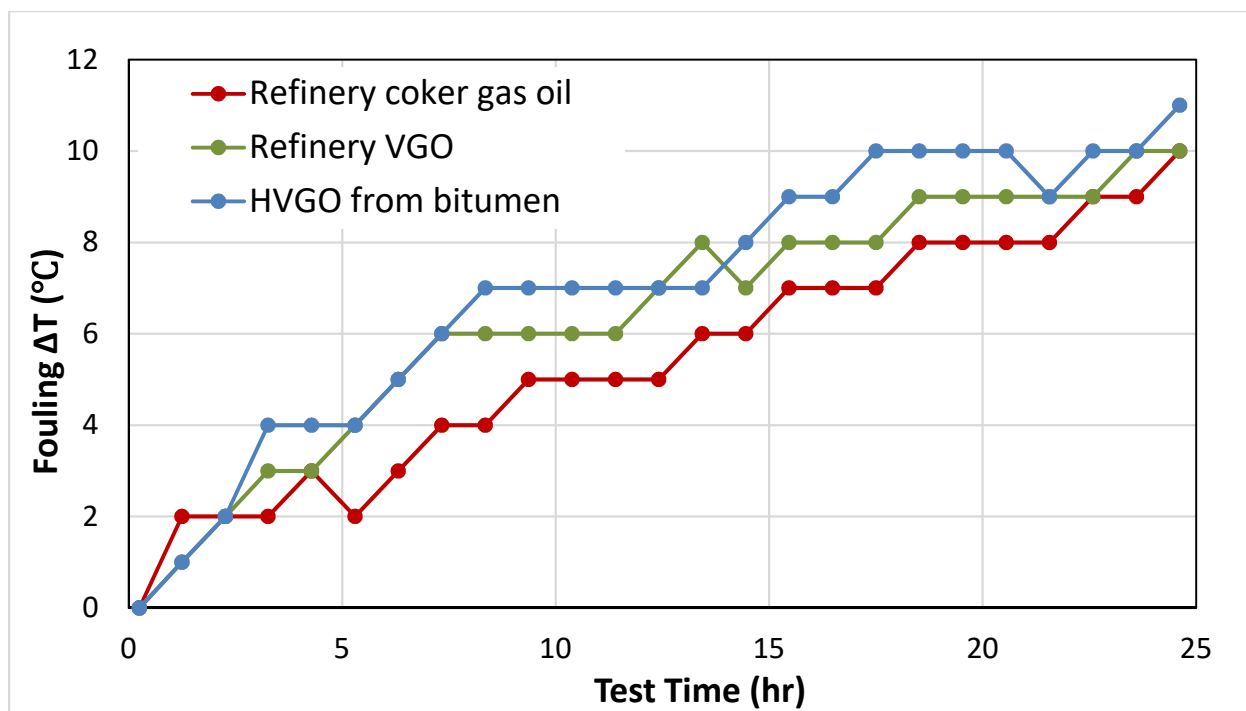


Figure 11 – Fouling tendency of refinery stream samples for different test times

6.4. CONCLUSIONS OF PHASE 3

Fouling tests were conducted with WCS-1 spiked with five model olefin compounds as well as their mixtures. The fouling tendencies of four different petroleum products were also tested. The experiments and results led to the following conclusions:

1. Fouling tendencies of WCS-1 spiked with model olefin compounds were in the low-fouling range and did not show any significant effects of the olefin content on fouling tendency.
2. Structure, type of olefin, boiling point, and mixing of olefins did not have significant effects on fouling tendencies.
3. Blending *n*-hexane with WCS-1 at the same ratio resulted in similar fouling tendency as WCS-1 spiked with model olefin compounds.
4. Fouling results of tested petroleum products (generated in-house or obtained from refineries) were in the range of low fouling.

7.0 OVERALL CONCLUSIONS

Through conducting fouling tendency measurements with WCS spiked with a number of selected olefins and diolefins, two of their mixtures, and with several petroleum fractions (with or without olefins), the following overall conclusions were derived:

- 1) There was no evidence for significant fouling due to olefins and diolefins.
 - Fouling tendencies of WCS spiked with selected olefin and diolefin compounds were in the low or low-medium fouling range and did not show any apparent effect of the olefin content on fouling tendency (up to 25 wt% olefins measured by H-NMR).
 - The molecular structure, type of olefin, and olefin boiling point did not have significant effects on fouling tendencies.
 - Mixtures of olefins and diolefins had fouling tendencies similar to those of individual olefins and diolefins.
 - Several oil fractions (with or without olefins) from refining operations or obtained by distillation of bitumen, and WCS containing olefins from thermally cracked bitumen, had low fouling tendencies.
- 2) When olefins were added to WCS, the main effect was due to diluent addition.
 - Diluting WCS with *n*-hexane resulted in fouling tendency similar to that of WCS spiked with olefins or diolefins at the same dilution ratio; *n*-hexane and *n*-hexene had very similar effects.
- 3) Thermally cracked bitumen showed high fouling tendency, which may be caused not only by light olefins but by other factors, such as olefins of higher molecular weight, asphaltene content, and stability of the material, or by synergies among these factors.

8.0 FUTURE WORK

After discussions among the steering committee members and with other stakeholders (oil sands producers who are developing partial upgrading technologies), it was proposed to organize a technical workshop to inform stakeholders of research findings from this project. The proposal of a workshop was strongly supported by Alberta Innovates and CanmetENERGY. In addition to discussing fouling caused by olefins and diolefins, and the pipeline specification on

olefin content, it was decided to discuss pipeline specifications in general for partially upgraded bitumen.

The workshop, titled “Workshop on Pipeline Specifications for Partially Upgraded Bitumen” was co-organized by Alberta Innovates and CanmetENERGY in Devon on January 22, 2019, in Calgary. The objectives of the workshop were: 1) to understand pipeline specifications for oil on olefins and other properties; 2) to inform stakeholders of the recent research results on olefins and thermally cracked products; 3) to understand the different viewpoints on the risks of shipping partially upgraded bitumen and potential changes to pipeline specifications.

About 50 participants attended the one-day workshop. In addition to the steering committee members, the research team members, and management from both Alberta Innovates and CanmetENERGY in Devon, the workshop participants included:

- Major oil sands producers that are developing partial upgrading technologies
- Petroleum refineries
- Major pipeline companies
- National Energy Board (NEB)
- Office of Energy Research and Development (OERD) of Natural Resources Canada
- Alberta Energy
- Alberta Petroleum Marketing Commission (APMC)
- CCQTA
- Other government agencies, research organizations, and industrial companies

During the workshop, the research results of this project were presented followed by interactive discussions, panel discussions, and round-table discussions. Various issues related to specifications for crude oil pipeline transportation were discussed: future research focus areas, engagement with stakeholders and regulatory bodies, refinery logistics, defining new parameters for partially upgraded bitumen, etc. These discussion notes are being compiled to form a document that will be shared with workshop participants, as well as other related stakeholders. It is expected that this workshop will promote further discussions and actions on revising the current pipeline specifications or defining new specifications for partially upgraded bitumen. The topics for future research work included:

- Investigate the relationship between P-value of cracked bitumen, and its fractions, and fouling;
- Study the synergetic effects between P-value of cracked materials and olefins.

In the meantime CanmetENERGY Devon's research team will develop a new research proposal to continue related research based on the above mentioned document, the feedback and recommendations from previous CCQTA meetings, and input from other conferences and scientific events. A short proposal will be prepared first, and the steering committee will review it to provide comments and suggestions before a more comprehensive proposal is developed for funding.

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10.0 REFERENCES

1. Fellows, G.K., Mansell, R., Schlenker, R., Winter, J. "Public-interest benefit evaluation of partial-upgrading technology", University of Calgary: School of Public Policy, January 2017.
2. Muse Stancil, "Assessment of opportunities for western Canadian partially upgraded heavy oil in Canadian refineries", August 2016.
3. Muse Stancil, "Canadian heavy oil crude competitiveness study Phase 2", October 2015.
4. PTAC, "Needs assessment for partial and field upgrading", March 2015.