



PROTECTED BUSINESS INFORMATION

FINAL REPORT

REDUCTION OF BITUMEN VISCOSITY FOR TRANSPORTATION BY H-DONOR ASSISTED VISBREAKING

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EXECUTIVE SUMMARY

This report is the final report on the project “Technology Development for Viscosity Reduction of Bitumen for Pipeline Transportation – H Donor–Assisted Visbreaking”, which was co-funded by CanmetENERGY and Alberta Innovates (AI) with sponsorship and support from Husky Energy and Alberta Sulphur Research Limited (ARSL).

Extensive pilot plant tests have been conducted with CanmetENERGY’s continuous pilot plant PP5 and batch autoclave PP8 units to study and demonstrate the H-donor assisted visbreaking of Canadian bitumen with synthetic crude oil (SCO) as the hydrogen donor. Various lab tests were performed with the feedstocks and products obtained from these pilot plant runs. The results of the pilot plant and lab tests provide a fundamental understanding of the SCO hydrogen donor assisted visbreaking and the required technical data for technology optimization and economic evaluation of large scale field demonstration and industrial commercialization.

The results of the PP5 continuous pilot plant tests are summarized as follows:

1. Four commissioning runs and 32 experimental runs were completed with CanmetENERGY’s PP5 pilot plant. Some operational issues (pressure buildup, coke formation, breaking of mixer shaft, etc.) occurred but were resolved without delaying progress of the project. The concept of hydrogen donor assisted visbreaking using SCO was tested in these runs under different operating conditions and with feedstocks having different bitumen/SCO blending ratios. All the runs conducted had reasonable mass balances within 100±5%.
2. Under the studied operating conditions and with either 5 or 12.5 vol% SCO feedstock, the visbreaking products did not meet the desired viscosity and density pipeline specifications of 350 cSt (at 7°C) and 19° API gravity, respectively. With 15 and 20 vol% SCO feedstocks, the viscosities of the visbreaking products reached values as low as 872 and 861 cSt (±56 cSt), quite close to the target of 350 cSt, while the API gravities of these products reached about 14.0° (±0.1°).
3. In most cases blending 5 wt% n-pentane into the visbreaking products obtained from the 15 and 20 vol% SCO feedstocks could easily achieve the viscosity target of 350 cSt.

4. The visbreaking products had TAN in the range of 1.00 to 1.70 mg KOH/g (± 0.02 mg KOH/g), which represents a significant reduction from that of the feedstocks (1.99 to 2.32 mg KOH/g). Their olefin contents were in the range of 1.0 to 2.3 wt% (± 0.03 wt%), depending on the visbreaking severity. The stabilities of the visbreaking products were reasonable with P-values (by Wiehe's method) in the range of 1.2 to 2.0. Sulphur contents were slightly decreased to the range of 3.68 to 4.46 wt% (± 0.03 wt%) from that of the feeds (3.98 ~ 4.50 wt%).
5. The naphtha fraction obtained from distillation of visbreaking product had a high olefin content of 10 to 12 wt%, which is understandable since most of the olefins formed during the visbreaking were molecules in the naphtha boiling range. The light gas oil fraction also had significant olefin content of 2.5 to 2.8 wt%, whereas the residue fraction had olefin content of 0.6 to 0.9 wt%. The light gas oil fraction had a lower TAN of 0.6 to 0.9 mg KOH/g, whereas the naphtha and the residue fractions had higher TANs of 1.1 and 2.4 mg KOH/g, respectively.
6. In the naphtha fraction, there were significant amounts of sulphides, mercaptans and thiophenes. In the total liquid product there were benzothiophene and its derivatives. The majority of the sulphur species could not be identified.
7. Under similar process operating conditions, a longer residence time resulted in higher visbreaking and decarboxylation reaction conversions, and therefore lower TAN (and higher product value). However the products were less stable (lower P-Value). Thus, there was a trade-off between TAN reduction and product stability. Higher pressure could help reduce olefin formation, and to a lesser extent, increase visbreaking conversion.

The results of the PP8 batch autoclave tests are summarized as follows:

1. Three sets of experiments were conducted in the batch autoclave reactor (PP8) to study:
 - a) TAN reduction kinetics, b) effect of different H-donor solvents, and c) effects of different soaking conditions, reaction temperature and SCO addition on liquid products properties. The batch autoclave was modified to accommodate inline sample collection of the reaction liquid to study TAN reduction kinetics.
2. Six runs were conducted to study the TAN reduction kinetics during soaking with two different feedstocks: 4 runs with an 85/15 (vol/vol) bitumen/SCO feedstock and 2 runs

with a raw bitumen feedstock. The experiments were conducted at soaking temperatures ranging from 360 to 390°C. Both feeds had similar TAN reduction trends with increased soaking time. Higher soaking temperatures (380 and 390°C) resulted in a greater TAN reduction rate than lower soaking temperatures (360 and 375°C), regardless of the feed used.

3. TAN reduction kinetics for the 85/15 bitumen/SCO feed followed zero order kinetics, with activation energy of 176.25 kJ/mol and pre-exponential factor of 1.3×10^{12} mg KOH/g.s. The TAN reduction in liquid product was consistent with CO and CO₂ yields, and can be explained by the extent of the decarboxylation of naphthenic acids.
4. Adding two different H-donor solvents of different hydrogen donation capabilities, tetralin and naphthalene, to the 85/15 bitumen/SCO feed did not have a significant impact on SARA and olefin contents of the liquid products. These tests were inconclusive since the presence of SCO as a hydrogen donor in the feed might have provided the required hydrogen donation capacity.
5. Six runs were conducted to study the effect of soaking, reaction temperature and SCO addition on visbreaking liquid products. Three runs were conducted with the raw bitumen feed and three were conducted with the 85/15 bitumen/SCO feed. For the raw bitumen feed, a higher visbreaking temperature (413°C) resulted in significantly lower product viscosity and TAN value, but higher toluene insolubles (indication of coke formation), due to the greater extent of decarboxylation of naphthenic acids and thermal cracking. The impact of soaking was not as significant as that of temperature. Higher temperature also resulted in higher total gas yield and higher yields of hydrogen, CO and CO₂, light hydrocarbons, and H₂S.
6. The 3 runs with the 85/15 bitumen/SCO feed were conducted at a reaction temperature of 413°C but with different soaking times. Increasing soaking time did not increase visbreaking conversion, but slightly improved the properties of the liquid products. The notable improvements were viscosity and TAN reductions achieved at the longest soaking time (40 minutes). The sulphur conversions were similar among the 3 runs, but higher than those achieved with the raw bitumen feed. The total gas yields among the 3 runs were comparable as they had similar visbreaking conversions.

7. Higher visbreaking conversion resulted in higher yields of naphtha and heavy gas oil. Light gas oil yield remained relatively constant.
8. While blending SCO directly with the liquid products obtained with the raw bitumen feed showed a dilution effect on the liquid properties, adding SCO, as an hydrogen donor, into raw bitumen as feed for visbreaking, resulted in significant reduction in viscosity compared to the direct blending of SCO with the visbreaking product of raw bitumen. The use of SCO as hydrogen donor promoted visbreaking in addition to the dilution effect.

CONTENTS

DISCLAIMER	i
COPYRIGHT	i
EXECUTIVE SUMMARY	ii
1.0 INTRODUCTION	1
2.0 BACKGROUND	2
3.0 PROJECT MANAGEMENT AND PROGRESS UPDATES	3
3.1. UNIT MODIFICATIONS AND PREPARATION	5
3.1.1. CONTINUOUS PILOT PLANT UNIT (PP5).....	5
3.1.2. BATCH AUTOCLAVE UNIT (PP8).....	6
3.2. FEEDSTOCKS	6
4.0 EXPERIMENTAL CONDITIONS, RESULTS AND DISCUSSION.....	8
4.1. CONTINUOUS PILOT PLANT UNIT (PP5).....	8
4.1.1. 15 vol% SCO SERIES	8
4.1.2. EXPERIMENTAL REPEATABILITY SERIES	20
4.1.3. 20 vol%, 12.5 vol% and 5 vol% SCO SERIES	22
4.2. AUTOCLAVE EXPERIMENTS.....	25
4.2.1. TAN REDUCTION KINETICS AT DIFFERENT SOAKING CONDITIONS.....	25
4.2.2. EFFECT OF HYDROGEN DONOR SOLVENTS ON VISBREAKING.....	29
4.2.3. EFFECT OF SOAKING, SCO ADDITION AND TEMPERATURE ON VISBREAKING	30
5.0 CONCLUSIONS.....	43
6.0 ACKNOWLEDGMENTS	46
7.0 REFERENCES	47

APPENDIX A: SIMDIS DATA OF FEEDSTOCKS AND PRODUCTS	48
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TABLES

Table 1 – Analytical tests results for bitumen and SCO feedstocks	7
Table 2 – Experimental conditions and product properties obtained with 15 vol% SCO feedstock	10
Table 3 – Olefin contents and TAN value of different distillation fractions from HS samples.....	16
Table 4 – Sulphur species in HS samples and a naphtha fraction	18
Table 5 – Experimental conditions and product properties of replicate runs with 15 vol% SCO feedstock.....	21
Table 6 – Experimental conditions and product properties obtained with feedstocks of 20, 12.5 and 5 vol% SCO.....	24
Table 7 – Olefin and SARA analysis results of visbreaking products with tetralin and naphthalene as H-donor	29
Table 8 – Variables and their levels of the experimental design of the autoclave experiments.....	30
Table 9 – Detailed operating conditions to study the effects of soaking, SCO addition and visbreaking reaction temperature	31
Table 10 – Autoclave test results to study the effects of soaking, SCO additions and visbreaking reaction temperature.....	33
Table 11 – Gas composition from GC analysis (raw bitumen feed).....	36
Table 12 – Gas yields of main components (raw bitumen feed)	37
Table 13 – Gas composition from GC analysis (15 vol% SCO feed)	40
Table 14 – Gas yields of main components (raw bitumen feed)	41

Table 15 – Comparison of liquid properties for SCO addition before and after visbreaking.....	43
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FIGURES

Figure 1 – Simplified flow diagram of PP5	5
Figure 2 – TAN reduction with time for the 15 vol% SCO feed and raw bitumen feed	27
Figure 3 – TAN reduction kinetics: experimental TAN values vs. model prediction	27
Figure 4 – Carbon dioxide yield with corresponding TAN reduction	28
Figure 5 – Temperature history of experiments to study the effects of soaking period and SCO addition on visbreaking	32
Figure 6 – Fractional yield of liquid products of raw bitumen feed and bitumen + SCO feed and total liquid products	42

1.0 INTRODUCTION

The extraction and upgrading of bitumen from oil sands are highly energy intensive with high capital and operational costs. There have been several critical challenges that hinder further oil sands development: 1) need for diluent and limited pipeline capacity; 2) low raw bitumen quality, reduced value and limited access to new markets; 3) high greenhouse gas (GHG) emissions and capital/operating costs for full upgrading. A significant portion of Alberta-produced bitumen is transported via pipeline by blending the high viscosity bitumen with diluent (25-30 vol%) to meet pipeline transportation specifications for viscosity (350 cSt at 7°C) and density (940 kg/m³ at 16.6°C). Apart from being expensive, diluent occupies valuable pipeline capacity and needs to be separated in refineries, only to be transported back for reuse. Raw bitumen is also sold at a discounted price on the world market and has very limited access to current or new markets due to its low quality.

A number of studies conducted by Alberta Innovates (AI) have shown that partial upgrading, especially if integrated with upstream operations, can effectively overcome these challenges, including reducing or even eliminating costly diluent use, increasing bitumen quality and market value, and significantly reducing GHG emissions and capital/operating costs, as compared to full bitumen upgrading. A goal has been set by AI to process 20% of in-situ produced bitumen through partial upgrading by 2030, which will potentially bring several billion dollars of net economic benefit to Alberta and Canada^{1,2,3,4}. Partial upgrading is a relatively simple process, as compared to full upgrading, by which bitumen from oil sands is treated only to a level such that it meets or exceeds the conditions for pipeline transportation in terms of density and viscosity, without (or with reduced) use of diluent. At the same time, other physical and chemical properties are also improved to some extent, such as total acid number (TAN) and asphaltene content, resulting in improved bitumen quality for refineries that would then be more willing to accept it as feedstock.

The goal of the national partial upgrading program (NPUP), led by CanmetENERGY in Devon (CanmetENERGY) and Alberta Innovates (AI), with the participation of a number of industrial companies, universities, and other government organizations, is to develop and demonstrate partial upgrading technologies for industrial scale-up and commercialization. The program also addresses other technical challenges related to the development and

implementation of partial upgrading technologies and to the acceptance of partially upgraded bitumen in domestic and international refineries. One of the first research projects under NPUP was to test and demonstrate the H (hydrogen)-donor assisted visbreaking concept for reducing bitumen viscosity to meet pipeline transportation specifications.

Four commissioning runs and 32 experimental runs were completed with the CanmetENERGY PP5 pilot plant unit. In addition, 3 sets of batch experiments were conducted with the CanmetENERGY PP8 (2-L autoclave) to increase the fundamental understanding of the chemistry of H-donor assisted visbreaking, and to provide supplementary information for guiding PP5 operation. This report summarizes all project activities, research findings and achievements since October 2015, with a focus on those from September to December of 2016.

2.0 BACKGROUND

There are a number of partial upgrading technologies at different stages of development, including HTL by Ivanhoe, HI-Q by MEG Energy, Jet Shear by Fractal Systems, and SCWC by JGC. All these technologies are based on thermal conversion and would require hydrogen addition as part of their process to hydrogenate olefin and diolefin compounds in order to meet the 1% total olefin content requirement for pipeline transportation. In locations where hydrogen availability is limited, hydrogenated upgrader or refinery streams that are capable of donating or transferring hydrogen to cap free radicals formed during thermal cracking, can be used instead of hydrogen gas.

In a recent investigation at ASRL in Calgary, Clark and Mercer⁵ used a 300-mL batch autoclave to study the thermal conversion of Athabasca bitumen with SCO derived from oil sands as the hydrogen donor. It is evident from the data that the presence of SCO had a noticeable positive effect on product distribution, possibly through its H-donor capability. It was shown in the study that other processing parameters might also influence the reaction pathway, including autoclave heating rate, soaking period and soaking temperature.

The work reported by Clark and Mercer was conducted in a batch autoclave unit which had the following limitations:

- Long heating and cooling times leading to inaccurate reaction kinetics

- Closed system leading to secondary reactions
- Poor material balance

The current project used a continuous pilot plant unit (PP5) and a batch autoclave unit (PP8) to determine if SCO can be used as an H-donor for visbreaking of Athabasca bitumen, if it could improve the process performance, and if so, to what extent. The project included the following:

- A systematic study on visbreaking (thermal processing) of bitumen in the presence of SCO (a proposed H-donor) using a continuous pilot plant and batch autoclave at various operating conditions and bitumen/SCO blending ratios.
- Optimization of process performance as a function of operation severity parameters (residence time and temperature) and bitumen/SCO blending ratios.
- A detailed product analysis and characterization to identify and quantify the effects of SCO as H-donor on pitch conversion and the physical and chemical properties of the partially upgraded bitumen product.

3.0 PROJECT MANAGEMENT AND PROGRESS UPDATES

An official project kick-off meeting was held at CanmetENERGY Devon on October 29, 2015. Three additional meetings were held at CanmetENERGY Devon on April 12, May 20, and August 18, 2016. Project update meetings were held (almost) monthly. Regular project updates were provided to project team members. The project team consisted of:

Jinwen Chen, CanmetENERGY	Shunlan Liu, AI
Adrian Majeski, CanmetENERGY	Nevin Flaming, AI
Ajae Hall, CanmetENERGY	Rodger Bernar, Husky Energy
Stephen Kieser, CanmetENERGY	Justin Jia, Husky Energy
Yi Zhang, CanmetENERGY	Peter Clark, ASRL
Mohamed Ali, CanmetENERGY	

In addition, Darren Mercer from ARSL and Tom Kemp from Husky Energy participated via tele-conference discussions at the monthly update meetings and through email communications.

Details from the project kick-off meeting and the first two update meetings were provided in the two previous progress reports. The following is a summary of the project update meeting held on August 18, 2016:

- During the mass balance period, the hot separator sample collection pail was open to the air at a temperature of about 80°C which meant that low boiling point products might have evaporated, resulting in a decreased product yield. Therefore sample collection was switched to a pressurized sampling bomb instead of a pail.
- Results showed that the soaking temperature was important to the performance of the visbreaking reactor so it was decided to maintain the soaking temperature at 380°C.
- The reactor mixer shaft broke after Run 24. The unit was shut down and cleaned. A temporary shaft made in-house was used until a new one could be acquired from the manufacturer (at least six weeks delivery time).
- In order to use the data generated from this project for further technology development and engineering design of a larger scale field demonstration plant, it is important to determine the repeatability and data reliability for the CanmetENERGY PP5 unit. Therefore, 4 replicates were performed over a week, to establish the margin of error and a baseline.
- According to previous test results for P values, the visbreaking products were at the lower end of the stability scale. Therefore, this precluded us from increasing the reaction severity. To improve results, it was agreed that the visbreaking reactor temperature should not exceed 420°C. Two sets of experiments were designed to test the limits of the reaction severity while maintaining reasonable product stability. One used a short residence time with high reaction temperature and the other used a long residence time and low reaction temperature.
- Husky suggested an experimental design of 32 runs varying four operating variables: visbreaking reactor temperature, residence time, bitumen/SCO ratio, and operating pressure (in the reactor) at two different levels. These tests would generate data to help in optimizing the process performance, designing and operating a larger scale field demonstration plant, and ultimately, the economic benefit of commercializing the technology. To reduce work load and optimize the budget, analytical tests

conducted on the product samples were limited to: P value, TAN, olefins content by NMR, viscosity at 7°C, density, off-gas yield and sulphur in total liquid product.

- The TAN reduction experiments conducted with the PP8 batch autoclave were reviewed. The TAN values of samples collected using an inline sample collection bomb at different time intervals showed a trend of decreasing TAN with reaction time at 380°C soaking temperature. It was agreed to continue testing the TAN reduction behavior at different soaking temperatures and with different hydrogen-donor solvents.

Research activities were determined based these decisions and suggestions.

3.1. UNIT MODIFICATIONS AND PREPARATION

3.1.1. CONTINUOUS PILOT PLANT UNIT (PP5)

CanmetENERGY's PP5 unit is a versatile unit that is typically used for continuous visbreaking (thermal cracking) and residue hydrocracking research. The plant can be run with either a tubular reactor or a continuous stirred tank reactor (CSTR). For this project it was used in CSTR mode to eliminate the temperature and concentration gradients present in tubular reactors. A simplified flow diagram of PP5 is shown in Figure 1. The detailed P&ID drawings are available and can be provided on request.

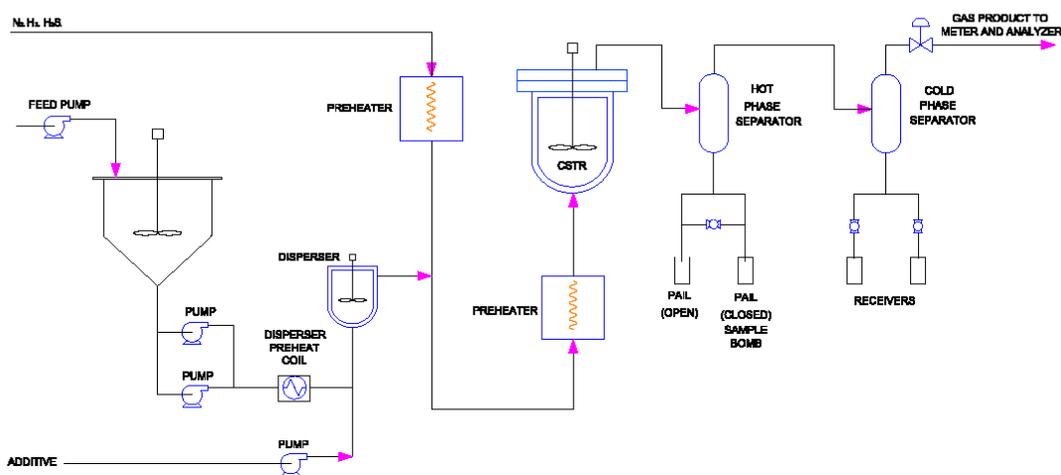


Figure 1 – Simplified flow diagram of PP5

Due to the particular operational requirements, the following modifications to the unit were made:

- Installed new coolant system around the reactor outlet;
- Installed new hot separator sampling bomb;
- Piping and instrumentation diagram (P&ID) updated;
- Checked, calibrated and installed all pumps;
- Calibrated liquid level-detectors;
- Checked and updated the safety control system and operation control programs;
- Updated and modified standard operating procedures (SOPs).

3.1.2. BATCH AUTOCLAVE UNIT (PP8)

CanmetENERGY's batch autoclave unit (PP8) is a 2-liter high-temperature high-pressure reactor. It is equipped with a stirrer to ensure homogenous distribution of the reacting materials and temperature, and a cooling coil that is used to quench the autoclave charge at the end of the reaction period. The temperature inside the autoclave is measured via three thermocouples at different heights. In the soaking and visbreaking tests and in the H-donor solvents tests, the unit was charged with the corresponding feedstock and the products were collected after a pre-defined reaction period. In the TAN reduction experiments, 30 ml-sample bombs were used to collect samples of the reacting liquid at different time intervals, in addition to the final liquid product collected after the autoclave was quenched.

3.2. FEEDSTOCKS

Two feedstocks were used: raw bitumen and synthetic crude oil (SCO) containing heavily hydrotreated gas oils from a bitumen upgrader. Thirty barrels of raw bitumen were provided by a producer in Alberta and Husky provided 10 barrels of SCO from its upgrader. The feedstocks used in these experiments were blends of these two at different ratios. The feedstock flowrates of the runs with PP5 were in the range of 0.5 to 2.0 kg/h, or 12 to 48 kg/day.

The raw bitumen and SCO feedstocks were sampled for various analyses; results are shown in Table 1. The detailed simulated distillation (SimDis) data for both bitumen and SCO are provided in Appendix A. As seen in Table 1, the properties of bitumen and SCO are similar to those in published literature.

Table 1 – Analytical tests results for bitumen and SCO feedstocks

Properties/Test	Method	Units	Bitumen	SCO
Density @15.6 C	ASTM D4052	g/ml	1.0150	0.8737
API gravity		°	8.0	30.4
Total acid number (TAN)	In-House	mg KOH/g	2.49	<0.10
Viscosity	ASTM D5018 (Bitumen) ASTM7042 (SCO)	cSt (bitumen) cP (SCO)	599.87 (80°C)	23.83 (7°C)
P-Value (bitumen)	Wiehe Method		2.82	
Compatibility (bitumen)				
IN (insolubility)			38.99	
SBN (Solubility blending number)			109.94	
TE (Toluene equivalence)		%	25	
VH (Volume of heptane)		mL	9.1	
Compatibility (SCO)	Wiehe Method			
Solvent oil equivalence			41	
Solubility of solvent oil			46.34	
SimDis	ASTM D7169 (bitumen) ASTM D2887Ext (SCO)			
IBP (0.5wt%)		°C	190.6	36.0
10wt%		°C	316.2	197.8
30wt%		°C	437.0	299.8
50wt%		°C	540.0	351.0
70wt%		°C	646.8	402.6
85wt%		°C	750.0	449.0
FBP (99.5wt%)		°C	-	561.0

4.0 EXPERIMENTAL CONDITIONS, RESULTS AND DISCUSSION

A total of 36 runs, including 4 commissioning runs and 32 experimental runs, were conducted with PP5. In addition, 3 sets of autoclave batch experiments were conducted with PP8. The results and discussion for the 4 commissioning runs and 9 of the experimental runs, as well as the 3 sets of autoclave batch experiments were provided in the two previous progress reports. This report focuses on the results and discussions of the remaining 23 PP5 experiments.

While SimDis tests were performed on a number of product samples at the beginning of this project (samples obtained from Runs 1 to 9), due to high cost and low usefulness of the SimDis data, it was decided that SimDis test would not be performed with product samples after Run 9.

4.1. CONTINUOUS PILOT PLANT UNIT (PP5)

4.1.1. 15 vol% SCO SERIES

The feedstock used for these 11 runs (Runs 10 to 20) had a bitumen/SCO blending ratio of 85/15 (vol./vol. %). These experimental runs were conducted between July 12 and August 13, 2016. Table 2 shows the process conditions and data from the analyses of the samples taken during these runs.

The soaker temperature was held at 380°C for Runs 10 to 14. The reactor bottom temperature was increased from 410 to 420°C for Run 10, 11 and 14. Since the P values of the products from previous runs were at the lower limit for stability, the reaction temperature was not raised. Instead, a shorter residence time combined with reaction temperature of 420°C for Run 12 was used to test the severity boundary. A lower pressure was tested for Run 13 as a lower pressure would save capital and operating costs for both field demonstration and commercial- scale plants. A lower soaker temperature of 340°C was tested for Runs 15 and 16 to compare product quality while the reactor temperature was held at 410°C and 415°C, respectively. A combination of lower reaction temperature and longer residence time was investigated in Runs 17 to 19, as a process operating option to reach product targets. For Run 20, the process conditions remained unchanged from those for Run 19 except that the hot separator temperature was increased from 200°C to 350°C, which forced the light liquid product coming out of the top of the hot separator to go into the cold separator. Since the main operating

conditions for Runs 19 and 20 were the same, a mass balance calculation was performed only for Run 19.

Generally the mass balances of these 11 runs were reasonable, being within $100\pm 5\%$, except for Run 10 and Run 16, as shown in Table 2. The instability of the feedstock flow rate (due to malfunctioning instrumentation) affected the accurate determination of the amount of feedstock pumped through the system during the mass balance period, which consequently resulted in the fluctuation of mass balance calculations.

The analytical data of the samples generated from these 11 runs, including the total liquid product (TLP), those taken from the soaker (S) and from the hot separator (HS), are listed in Table 2. They are noted by -TLP, -S, -HS, respectively, after the run number. In addition, 3 liquid product samples were prepared by proportionally blending certain amounts of n-pentane, which was estimated by online GC gas analysis data, into the corresponding HS samples. These were designated as 10-FP-5%, 11-FP-5%, and 12-FP-5% for Runs 10, 11 and 12, respectively.

Table 2 – Experimental conditions and product properties obtained with 15 vol% SCO feedstock

Sample ID	Feed	10-S	10-HS	10-FP -5%	11-HS	11-TLP	11-FP -5%	12-S	12-HS	12-TLP	12-FP -5%	13-S	13-HS	
Soaker bottom temp. (°C)	-	380			380			380				380		
Reactor bottom temp. (°C)	-	415			420			420				420		
Reactor time (min)	-	16			16			14				14		
Pressure (psi)	-	750			750			750				500		
Mass balance (%)	-	105.7			97.2			104.8				101.5		
Viscosity (cSt)	7°C	-	-	1229	313	973	1020	295	-	1636	1217	359	-	2387
	60°C	549	213	-	-	-	-	-	225	-	-	-	258	-
TI (wt%)	0.06	0.05	0.04	-	0.03	-	-	0.05	0.02	-	-	0.11	0.04	
Density @15.6°C (g/mL)	0.9928	-	0.9733	0.9519	0.9714	0.9721	0.9515	-	0.9755	0.9717	0.9525	-	0.9775	
API (°)	11	-	13.9	17.2	14.2	14.1	17.2	-	13.6	14.1	17.1	-	13.3	
TAN (mg KOH/g)	2.32	2.14	1.44	-	1.41	-	-	2.05	1.48	-	-	2.03	1.54	
Total olefin (wt% 1-decene by NMR)	-	-	1.93	-	2.26	-	-	-	1.96	-	-	-	2.11	
P Value	-	-	1.46	-	-	-	-	-	1.54	-	-	-	-	
Insolubles C5 (wt%)	15.21	-	-	-	-	-	-	-	12.47	-	-	-	-	
MCR (wt%)	12.04	-	-	-	-	-	-	-	12.38	-	-	-	-	
Sulphur XRF (wt%)	4.28	-	-	-	-	-	-	-	3.96	-	-	-	-	

Table 2. continued

Sample ID	14-S	14-HS	15-S	15-HS	16-HS	17-S	17-HS	18-S	18-HS	19-HS	19-FP -1%	19-FP -3%	20-HS	
Soaker bottom temp. (°C)	380		340		340	380		380		380			380	
Reactor bottom temp. (°C)	410		410		415	400		390		400			400	
Reactor time (min)	16		16		16	32		42		42			42	
Pressure (psi)	750		750		750	500		500		500			500	
Mass balance (%)	101.5		102.0		92.3	103.3		101.9		103.0			-	
Viscosity (cSt)	7°C	-	1924	-	3305	2926	-	1405	-	1379	872	722	431	1428
	60°C	232	-	458	-	-	138	-	111	-	-	-	-	-
TI (wt%)	0.1	0.07	0.13	0.05	0.01	0.34	0.02	0.38	0.01	0.02	-	-	-	
Density @15.6°C (g/mL)	-	0.9752	-	0.9793	0.9787	-	0.9754	-	0.9743	0.9723	-	-	0.9795	
API (°)	-	13.6	-	13	13.1	-	13.6	-	13.7	14	-	-	13	
TAN (mg KOH/g)	2.03	1.57	2.27	1.69	1.67	1.88	1.28	1.79	1.17	1.04	-	-	1.04	
Total olefin (wt% 1-decene by NMR)	-	1.88	-	1.43	1.84	-	2.87	-	1.56	1.98	-	-	1.51	
P Value	-	-	-	-	-	-	1.46	-	1.38	1.26	-	-	-	
InsolublesC5 (wt%)	-	12.27	-	-	-	-	12.3	-	12.41	12.74	-	-	-	
MCR (wt%)	-	12.69	-	-	-	-	12.72	-	12.75	13.19	-	-	-	
Sulphur XRF (wt%)	-	3.94	-	-	-	-	3.88	-	3.89	3.86	-	-	-	

As noted in previous reports, a small amount of light hydrocarbons (C4 to C8) could not be condensed into liquid and therefore, became part of the off gas stream fraction. Although the amount was relatively small (around 5%), it could have a significant impact on the viscosity of the TLP. Since the process operating conditions used in previous runs could not generate visbreaking products that fully met the density and viscosity specifications for pipeline transportation, the impact of adding a small amount of *n*-pentane to HS samples was investigated. Five HS samples were selected for addition of certain amounts of *n*-pentane as diluent. These samples were designated as -FP-x% before the run number, where FP represents final liquid product and x% represents the weight percentage of *n*-pentane added into the HS sample. These samples were 10-FP-5%, 11-FP-5%, 12-FP-5%, 19-FP-1%, and 19-FP-3%.

In general the viscosity reduction for these 11 runs was significant (Table 2). At 7°C, the viscosities of the HS and TLP samples ranged from 872 to 3305 cSt (at 7°C), depending on the operating conditions in the soaker and the reactor. The API gravities ranged from 13 to 14° for these samples. It can be seen in Table 2 that most of the samples had toluene insolubles (TI) values below 0.1 wt%. Given the measurement error and the TI value of the feed (0.06 wt%), these samples would not be considered to contain coke. The TI values of two soaking samples (17-S and 18-S) were 0.34 and 0.38 wt%, respectively, indicating that minor coking occurred in the soaking vessel, which could lead to long-term coke build-up in both the soaking vessel and visbreaking reactor under the conditions used in these 2 runs. The TAN reduction was quite significant, from 2.32 mg KOH/g in the feed to as low as 1.04 mg KOH/g, with most of the samples having a TAN below 2 mg KOH/g. In general the higher the reduction in viscosity (or in pitch conversion), the higher the reduction in TAN that was observed.

It is seen in Table 2 that the 3 samples to which 5 wt% *n*-pentane was added (10-FP-5%, 11-FP-5%, and 12-FP-5%) had viscosities below or just above 350 cSt (at 7°C), meeting the pipeline specification for viscosity. Their API gravity was about 17°, close to the pipeline specification of 19°. The samples in which 1 and 3 wt% *n*-pentane was added (19-FP-1% and 19-FP-3%, respectively) had viscosities of 722 and 431 cSt (at 7°C), respectively, close to the viscosity pipeline specification (API gravities were not measured for these two samples).

The P value, the contents of total olefin, asphaltene (C5 insolubles), micro carbon residue (MCR), and sulphur content, were measured for selected HS samples as shown in Table 2. The

total olefin contents were in the range of 1.43 to 2.26 wt% (sample 17-HS might have been contaminated since it had unusual high total olefin content of 2.87 wt%), with values increasing as viscosity decreased, or pitch conversion increased. This was expected due to the increased thermal cracking. Clearly the addition of SCO as hydrogen donor could not generate visbreaking products with total olefin content below 1 wt%, and therefore, further olefin removal would be needed to meet the pipeline specification of 1 wt% for olefin. Note that the feedstock used for these 11 runs had bitumen/SCO ratio of 85/15 (vol/vol %). The MCR content was relatively constant, ranging from 12 to 13 wt% for the 5 selected HS samples (12-HS, 14-HS, 17-HS, 18-HS, and 19-HS), meaning that hydrogen donation suppressed coke formation during visbreaking reactions. It is also noted in Table 2 that asphaltene content (C5 insolubles) decreased from 15 wt% in the feed to around 12.5 wt% for the same 5 HS samples, which contributed to the observed reduction in viscosity for these samples. The total sulphur content was reduced slightly from 4.3 wt% in the feed to around 3.9 wt% for these samples, indicating a minor desulphurization during visbreaking. The P values of these samples ranged from 1.26 to 1.54, indicating moderate stabilities of these samples.

The effect of soaker temperature on visbreaking was investigated through two set of runs, Runs 10 and 16, and Runs 14 and 15 as shown in Table 2. Runs 10 and 16 were conducted with soaker temperature of 380 and 340°C, respectively, with constant reactor temperature of 415°C. Runs 14 and 15 were conducted with soaker temperature of 380 and 340°C, respectively, with constant reactor temperature of 410°C. It is thought that a higher soaker temperature favors the formation of hydrogen radicals from the hydrogen donors, resulting in a greater reduction in viscosity, density and TAN. Indeed such trends were observed for these two sets of runs. For example, the viscosity, API gravity, and TAN of 16-HS were 2926 cSt (at 7°C), 13.1°, and 1.67 mg KOH/g, respectively, while those of 10-HS were 1229 cSt (at 7°C), 13.9°, and 1.44 mg KOH/g, respectively. However, the total olefin content showed an increasing trend with soaker temperature, from 1.84wt% for 16-HS to 1.93wt% for 10-HS, due to increased thermal cracking, as mentioned earlier.

A higher reactor temperature also resulted in an increased reduction in viscosity, density and TAN as can be seen by comparing the results of Runs 15 and 16 and those of Runs 10, 11 and 14 (Table 2). Runs 15 and 16 were conducted at reactor temperature of 410 and 415°C, respectively, with constant soaker temperature of 340°C. Runs 10, 11 and 14 were conducted at

reactor temperature of 415, 420, and 410°C, respectively, with constant soaker temperature of 380°C. For example, 15-HS had viscosity, API gravity, and TAN values of 3305 cSt (at 7°C), 13°, and 1.69 mg KOH/g, respectively, while 16-HS had values of 2926 cSt (at 7°C), 13.1°, and 1.67 mg KOH/g, respectively. Similarly, increased reactor temperature also resulted in increased total olefin content, from 1.43 wt% for 15-HS to 1.84 wt% for 16-HS for the same reason as mentioned earlier.

To test the severity boundary (lower and upper limits) for the visbreaking reactor operating conditions, two sets of experiments were run. One set had a shorter residence time (16 and 14 min) at a high reaction temperature (420°C) (Runs 11 and 12) and the other set used a longer residence time (32 and 42 min) at a lower reaction temperature (400°C) (Run 17 and 19). Run 11 achieved a viscosity of 973 cSt (at 7°C) with a high olefin content of 2.26 wt%. A slight decrease in residence time from 16 min to 14 min for Run 12 resulted in a sharp increase in viscosity to 1636 cSt while the olefin content was reduced to 1.96 wt%. It was concluded that the combination of high temperature and short residence time would not be a desired operation mode due to the high olefin content in the product. An increase in residence time from 32 min for Run 17 to 42 min for Run 19 resulted in decreased viscosity from 1403 cSt to 872 cSt, respectively. TAN was also reduced from 1.28 mg KOH/g for Run 17 to 1.04 mg KOH/g for Run 19 while a slight decrease in stability P value was observed, from 1.46 to 1.26, due to the slight increases in asphaltene and MCR contents in the latter run.

The product generated from Run 19 had a viscosity of 872 cSt (at 7°C), similar to that from Run 11 (973 cSt), but with a slightly lower olefin content of 1.98 wt%, compared to 2.26 wt% for Run 11. This indicates that a combination of long residence time and low temperature resulted in better product quality than that of short residence time and high temperature: there is always a trade-off between product viscosity, olefin content, TAN and stability. An optimized combination of reaction temperature and residence time should be determined based on not only product quality and properties, but also on capital and operating costs that are dependent on reactor size, energy requirements, etc.

The effect of reaction pressure on the hydrogen donor assisted visbreaking was also investigated through Runs 12 and 13 by changing the pressure in the reactor while maintaining other operation conditions constant. As seen in Table 2, the density and TAN of 12-HS and 13-

HS were quite similar. However 12-HS, obtained at pressure of 750 psi, had a significantly lower viscosity than that of 13-HS, obtained at 500 psi, indicating that increased pressure improved viscosity reduction. Higher pressure forces more reacting molecules to remain in the liquid phase to form free radicals and hydrogen-donor atoms available for abstraction. The hydrogen abstraction step is more favourable in the liquid phase compared to the gas phase, therefore, a high concentrations of free radicals and hydrogen-donor atoms in the liquid phase at higher pressure increases the extent of thermal cracking and pitch conversion, hence reducing viscosity. This positive effect might have been caused by the increased light hydrocarbon condensing in the liquid product (equivalent to adding additional light hydrocarbons into the product) by the phase equilibrium effect. It was also noted that 12-HS had a slightly lower total olefin content than that of 13-HS. This effect was also observed with the products obtained with other feedstocks of different bitumen/SCO ratios, as will be discussed shortly. Higher availability of hydrogen donor atoms for abstraction in the liquid phase can also explain the difference in olefin content in Runs 12 and 13, where the higher pressure run (Run 12) had lower olefin content of 1.96 wt% compared to that of 2.11 wt% for Run 13. Another possible explanation is that increased pressure prevented overcracking of light hydrocarbons in the vapor phase, which is considered the main cause of olefin formation.

Table 3 – Olefin contents and TAN value of different distillation fractions from HS samples

Sample	Boiling range (°C)	6-HS			18-HS			19-HS		
		Distillation yield (wt%)	TAN (mg KOH/g)	Total olefin content (wt%1-decene by NMR)	Distillation yield (wt%)	TAN (mg KOH/g)	Total olefin content (wt%1-decene by NMR)	Distillation yield (wt%)	TAN (mg KOH/g)	Total olefin content (wt% 1-decene by NMR)
HS product	IBP-FBP		1.40	1.94		1.17	1.56		1.04	1.98
Naphtha	IBP-200	6.33	2.42	12.58 (11.90)	5.90	1.14 (1.19)	10.52	6.07	1.19	10.98 (12.42)
Light gasoil	200-343	21.81	0.92	2.78 (2.63)	17.65	0.64 (0.67)	2.52	19.60	0.57	2.64 (2.99)
Residue	343-FBP	70.64	1.46	0.89 (0.84)	75.08	1.24 (1.30)	0.64	73.17	1.16	0.75 (0.85)
Water		0.13			0.36			0.45		
Loss		1.09			1.01			0.70		
Calculated contents		100	1.40	2.05 (1.94)	100	1.12 (1.17)	1.56	100	1.04	1.75 (1.98)
Mass balance			100%	105.7% (1005)		95.7% (100%)	100%		100%	88.4% (100%)

To further determine how the olefins and acids (measured as TAN) in the visbreaking product were distributed along the boiling range, the product samples 6-HS (from Run 6, also discussed in the project progress report of September 2016), 18-HS (from Run 18) and 19-HS (from Run 19) were chosen to undergo a distillation to obtain the naphtha, light gas oil, and residue fractions. The samples of these fractions were subsequently analyzed for olefin content and TAN. Table 3 shows the distillation fractions, their boiling ranges, distillation yields, olefin contents, and TAN. Mass balance calculations were conducted for olefin content and TAN by comparing their total contents in 6-HS, 18-HS and 19-HS with the sum of the normalized (to exclude loss) individual contents of the three fractions at their corresponding distillation yields. Among the 6 mass balance calculations for olefin content and TAN, three of them, TAN for Runs 6 and 19 and olefin content for Run 18, were 100% where the other three had mass balance calculations were as low as 88.4% and as high as 105.7%. If it is assumed that the total olefin content in the HS samples is accurate and distillation losses are evenly distributed among the three fractions, then the errors in the mass balance can be evenly distributed among the olefin content of the three fractions. Therefore a second normalization on the olefin content and TAN can be done to get 100% mass balance calculations. The values of the normalized TAN and olefin content are shown in Table 3 in the parentheses.

The total olefin contents and TAN of the three HS products were 1.94, 1.56, and 1.98 wt%, and 1.4, 1.17 and 1.04 mg KOH/g, for Runs 6, 18 and 19, respectively (Table 3). After distillation, the olefin content in the naphtha fractions from these three runs ranged from 10.52 wt% to 12.58 wt% with Run 6 naphtha having the highest olefin content. The olefin contents were in the range of 2.52 to 2.78 wt% in the light gas oil fraction, with that from Run 6 having the highest. The residue fractions had olefin contents in the range from 0.64 to 0.89 wt%, all being less than 1 wt%. Such an olefin distribution trend is understandable and expected since most of the olefin molecules generated during the visbreaking were light hydrocarbons concentrated in the naphtha boiling range, with some in the light gasoil boiling range. Even the residue fractions had noticeable olefin contents of around 0.7 wt%, although these big olefin molecules are not expected to cause fouling and other operating issues in downstream refining. This olefin distribution trend in the visbreaking products means that both the naphtha and light gasoil fractions (or IBP to 343°C inclusive) in the visbreaking products would need olefin reduction to 1 wt% or below in order to ensure the 1 wt% total olefin content specification for

pipeline transportation after post-treatment blending. The approaches and technologies for olefin reduction or removal are beyond the scope of this project and will not be discussed in this report.

The TAN values of the three HS products were 1.40, 1.17 and 1.04 mg KOH/g, for Runs 6, 18 and 19, respectively (Table 3). The TAN values in the 3 fractions showed a similar trend for the three samples, but different from that of olefin content. The naphtha and the residue fractions had higher TAN values than the light gas oil for all three runs. This TAN distribution trend is quite interesting. There are several factors that contribute to TAN in the visbreaking products, such as naphthenic acids, and heteroatoms such as sulphur and nitrogen, which contain protons, and/or chloride in the form of hydrochloric acid, etc. The observed high TAN in the naphtha fraction is mainly due to reactive sulphur compounds, such as mercaptans and sulphides, as will be discussed shortly. The high TAN in the residue fraction is most likely caused by naphthenic acids. Nevertheless if hydrotreating is used to saturate the olefins and diolefins in the naphtha fraction (or the combined naphtha and light gas oil fractions), TAN will be effectively reduced at the same time.

Table 4 – Sulphur species in HS samples and a naphtha fraction

Analysis	18-HS	19-HS	Naphtha from 19-HS	Units
Carbonyl sulphide	<0.7	<0.7	-	mg/kg
Hydrogen sulphide	117.1	89	40.00	mg/kg
Methyl mercaptan	<0.7	<0.7	87.76	mg/kg
Ethyl mercaptan	<0.7	<0.7	86.32	mg/kg
Dimethyl sulphide	<0.7	<0.7	-	mg/kg
Carbon disulphide	<0.7	<0.7	-	mg/kg
Isopropyl mercaptan	<0.7	<0.7	129.76	mg/kg
tert-Butyl mercaptan	<0.7	<0.7	-	mg/kg
<i>n</i> -Propyl mercaptan	<0.7	<0.7	120.14	mg/kg
Ethyl methyl sulphide	<0.7	<0.7	-	mg/kg
<i>sec</i> -Butyl mercaptan	<0.7	<0.7	-	mg/kg
Isobutyl mercaptan	<0.7	<0.7	-	mg/kg
Thiophene	32.1	38.3	336.66	mg/kg
Diethyl sulphide	<0.7	<0.7	-	mg/kg

Analysis	18-HS	19-HS	Naphtha from 19-HS	Units
<i>n</i> -Butyl mercaptan	<0.7	<0.7	43.53	mg/kg
Dimethyl disulphide	<0.7	<0.7	-	mg/kg
2-Methylthiophene	306.6	327	3321.49	mg/kg
3-Methylthiophene	111.8	121.5	1137.63	mg/kg
Diethyl disulphide	16.5	<0.7	-	mg/kg
Benzothiophene	197.7	207.7	-	mg/kg
5-Methylbenzothiophene	124.7	128.1	-	mg/kg
3-Methylbenzothiophene	297	309.5	63.26	mg/kg
Diphenyl sulphide	216.2	269.7	-	mg/kg
Sulphur species detected	1419.7	1490.8	5366.5 (representing 327.9 in 19-HS)	mg/kg
Total sulphur (By XRF)	3.89	3.86	1.78	wt%
Note: '-' means "not detected"				

To understand which sulphur species are present in the visbreaking products and in the naphtha fractions, a modified version of ASTM D5623 test was used to obtain the detailed sulphur speciation in these materials. The test was based on two-dimensional gas chromatography (2D-GC) and extended to the whole boiling range of the liquid products⁶. The data for 18-HS, 19-HS, and the naphtha fraction from 19-HS are shown in Table 4. Table 4 lists all the standards for sulphur species available at CanmetENERGY Devon. As seen in the table, the major sulphur species detected in the naphtha fraction were sulphides, mercaptans and thiophenes, comprising 0.54 wt% (or 5366.5 mg/kg) sulphur content. The total sulphur content measured by XRF for the naphtha fraction was 1.78 wt%, meaning that less than one third of the total sulphur could be identified and quantified. For 18-HS and 19-HS, the detected sulphur species totaled only 0.14 and 0.15 wt% (1419.7 and 1490.8 mg/kg), respectively, which was a small portion of the total sulphur content as measured by XRF (3.89 and 3.86 wt%, respectively). With more sulphur standards being acquired in the future, this in-house modified ASTM D5623 method will provide improved quantitative information on sulphur speciation in oil samples

4.1.2. EXPERIMENTAL REPEATABILITY SERIES

To ensure confidence in the PP5 unit operation, and to validate the accuracy and reliability of the experimental data, four runs were completed between September 20 and 23, 2016 under the same operating conditions (those of Run 18). Table 5 lists the process conditions, the mass balance calculations, and analytical results. The feed used for these 4 runs (Runs 21 to 24) had a bitumen/SCO ratio of 85/15 (vol/vol). The mass balances were reasonable, being within $100\pm 5\%$, with an average of 102.9% and standard deviation of 1.5%.

As seen in Table 5, the analytical data for the samples from the 4 runs, viscosity, density, TAN, olefin content, P value, and sulphur content, were quite close to each other, indicating that experimental procedures, product sampling and handling, and sample analyses were consistent. The small variations were considered to be within experimental error. The standard deviations of these measurements are listed in Table 5 as well.

The reactor mixer shaft was found to be broken after Run 24. The unit was shut down and cleaned. A small amount of coke was found at the bottom and inner wall of the reactor. To continue the experiments a replacement shaft was built in-house and installed.

Table 5 – Experimental conditions and product properties of replicate runs with 15 vol% SCO feedstock

Sample ID	Feed	21-S	21-HS	22-S	22-HS	23-S	23-HS	24-S	24-HS	Average	Standard deviation	
Soaker bottom temp. (°C)	-	380		380		380		380				
Reactor bottom temp. (°C)	-	390		390		390		390				
Reactor time (min)	-	42		42		42		42				
Pressure (psi)	-	500		500		500		500				
Mass balance (%)	-	103.2		102.0		104.9		101.5				
Viscosity (cSt)	7°C	-	-	974	-	971	-	1063	-	1099	1027	55.7
	60°C	564	138	-	143	-	130	-	-	-	137	5.4
TI (wt%)	0.02	0.03	0.05	0.06	0.03	0.12	0.03	0.08	0.12	0.06	0.04	
Density @15.6°C (g/mL)	0.9933	0.9825	0.9748	0.9828	0.9734	0.9849	0.9752	0.9828	0.9742	0.9744	0.00007	
API (°)	11.0	12.5	13.7	12.5	13.9	12.2	13.6	12.5	13.8	13.8	0.1	
TAN (mg KOH/g)	2.2	-	1.15	-	1.20	-	1.17	-	1.18	1.18	0.02	
Total olefin (wt% 1-decene by NMR)	-	-	1.72	-	1.74	-	1.78	-	1.70	1.74	0.03	
P-Value	-	-	1.26	-	-	-	-	-	-			
Sulphur XRF (wt%)	4.24	-	3.77	-	3.82	-	3.86	-	3.79	3.81	0.03	

4.1.3. 20 vol%, 12.5 vol% AND 5 vol% SCO SERIES

A total of 8 runs (Runs 25 to 32) were completed between October 13 and December 9, 2016, with feedstocks with 80/20, 87.5/12.5 and 95/5 bitumen/SCO blending ratios (vol/vol). These runs were conducted to investigate the effect of bitumen/SCO blending ratio on visbreaking performance and product quality by keeping the soaker and reactor temperatures constant at 380°C and 395°C, respectively. The detailed operating conditions and properties of the visbreaking products obtained from these runs are listed in Table 6. As seen in Table 6, all runs had satisfactory mass balances, being within 100±3%.

Runs 25 and 26 were conducted with a 80/20 bitumen/SCO ratio feedstock. Run 25 had a longer residence time (51 min) under lower pressure (550 psi) while Run 26 had a shorter residence time (32 min) under higher pressure (900 psi). The combination of a longer residence time with lower pressure (Run 25) resulted in a greater reduction in density, sulphur content, viscosity and TAN than the combination of a shorter residence time and higher pressure (Run 26). On the other hand, the former resulted in higher total olefin content (higher pitch conversion) and reduced product stability (P value) than the latter. The positive effect of longer residence time was also observed with Runs 27 and 28, which were conducted with the 87.5/12.5 bitumen/SCO feedstock under much reduced pressure (200 psi) with residence times of 16 and 46 min, respectively. A similar positive effect of residence time was also seen for Runs 31 and 32, which were conducted with the 95/5 bitumen/SCO feedstock at 550 psi and with residence times of 16 and 51 min, respectively. The positive effect of pressure on the reductions of density, viscosity, sulphur, and TAN are illustrated by Runs 29 and 30, which were conducted with the 95/5 bitumen/SCO feedstock at a residence time of 32 min, and pressures of 200 and 900 psi, respectively. The increased pressure resulted in slightly reduced total olefin formation (Runs 29 and 30), which was also observed with Runs 12 and 13, as discussed earlier in Section 4.1.1.

The visbreaking products obtained with the 80/20 bitumen/SCO feedstock (25-HS and 26-HS) had much lower viscosities, densities and sulphur contents than those obtained with the 95/5 bitumen/SCO feedstock (30-HS and 32-HS) under similar operating conditions (Table 6). This improvement might have been the result of two factors: the dilution effect of the additional 15 vol% SCO added to the former and the increased visbreaking conversion and hydrogen transfer due to the additional 15 vol% SCO. The trade-off would be the increased operating cost

of the additional 15 vol% SCO, a factor that has to be considered in an economic evaluation for commercialization. The increased SCO content in the feed may have slightly reduced olefin formation, from 1.32 wt% for 30-HS to 1.18 wt% for 26-HS. The TAN value and stability P value were not affected by the increased SCO content as shown with Runs 26 and 30.

Comparing Runs 25 to 32, Run 25 yielded the best visbreaking product with a viscosity of 861 cSt (at 7°C) and API gravity of 14.5°, close to pipeline specifications.

PP05 was shut down after Run 29 on November 23, 2016, due to an increased pressure drop in the reactor. It was found, after the reactor was opened, that the top of the reactor mixer shaft had corroded. A small amount of coke was also found at the bottom and the inner wall of the reactor. The reason for the corrosion was that the temporary mixer shaft had been made using carbon steel. A replacement mixer shaft made with 316- stainless steel was built and installed to complete Runs 30 to 32.

Table 6 – Experimental conditions and product properties obtained with feedstocks of 20, 12.5 and 5 vol% SCO

Sample ID	20 vol% Feed	25-HS	26-HS	12.5 vol% Feed	27-HS	28-HS	5 vol% Feed	29-HS	30-HS	31-HS	32-HS	
Soaker bottom temp. (°C)	-	380	380	-	380	380	-	380	380	380	380	
Reactor bottom temp. (°C)	-	395	395	-	395	395	-	395	395	395	395	
Reactor time (min)	-	51	32	-	16	46	-	32	32	16	51	
Pressure (psi)	-	550	900	-	200	200	-	200	900	550	550	
Mass balance (%)	-	103.0	97.1	-	102.3	99.2	-	102.0	102.3	101.2	100.8	
Viscosity (cSt)	7°C	-	861	1313	-	14719	3271	-	11571	4580	15974	2414
	60°C	371	-	-	720	-	-	1428	-	-	-	-
TI (wt%)	0.03	0.04	0.01	0.02	0.03	0.02	0.04	0.01	0.02	0.02	0.04	
Density @15.6°C (g/mL)	0.9868	0.9692	0.9712	0.9990	0.9880	0.9826	1.0010	0.9934	0.9887	0.9933	0.9847	
API (°)	11.9	14.5	14.2	10.1	11.7	12.5	9.9	10.9	11.6	11	12.2	
TAN (mgKOH/g)	1.99	1.06	1.20	2.19	1.53	1.06	2.32	1.31	1.28	1.64	0.9	
Total olefin (wt% 1-decene by NMR)	-	1.36	1.18	-	1.05	1.55	-	1.39	1.32	1.15	1.29	
P-Value	-	1.26	1.46	-	2.10	1.54	-	1.82	1.5	1.98	1.26	
Sulphur XRF (wt%)	3.98	3.68	3.76	4.38	4.17	4.02	4.56	4.38	4.35	4.46	4.22	

4.2. AUTOCLAVE EXPERIMENTS

A number of autoclave experiments were conducted with CanmetENERGY's PP8 to complement the PP5 tests. Three sets of experiments were completed: 1) 6 runs to test TAN reduction kinetics at different soaking conditions; 2) 2 runs to study the effects of hydrogen donor solvents on the visbreaking process; and 3) 6 runs to investigate the effect of soaking periods, SCO addition and visbreaking temperature on total liquid product properties.

4.2.1. TAN REDUCTION KINETICS AT DIFFERENT SOAKING CONDITIONS

To study the TAN reduction kinetics it was necessary to collect multiple samples at different times from the same experiment. The PP8 autoclave was modified to allow for inline sampling during the operation with minimum operation interruption. The 85/15 bitumen/SCO feedstock used in PP5 experiments was used for this study (total of 4 runs). The raw bitumen without SCO addition was also used (total of 2 runs). The feed was heated in the autoclave to soaking temperatures of 360, 375, 380 and 390°C for the 15 vol% SCO feed, and to 360 and 380°C for the raw bitumen feed. In these six runs, the first sample was taken when the reactor temperature reached 350°C, and successive samples were taken every 10 min after 350°C was reached, except for Run 2 in which the first sample was taken at 355°C. In addition to the 6 TAN reduction runs, an exploratory run was conducted at 415°C, at which temperature visbreaking is actually occurring, rather than soaking. This run was conducted to test the newly installed inline sampler and to provide operating guidelines to achieve lower soaking temperatures.

Six or seven samples were collected from each of the 6 runs and were analyzed for TAN. Figure 2 shows the TAN reduction with time for the 6 runs. In the figure, time zero is that for the collection of the first sample. The 4 runs with 15 vol% SCO feed (dotted lines in Figure 2) showed a similar trend of TAN reduction with time. TAN reduction also was greater with increased soaking temperature. At low soaking temperatures, 360 and 375°C, the TAN reductions were similar, and the slopes of the TAN with time curves were much flatter than those at high temperatures, 380 and 390°C, indicating a much decreased TAN reduction rate. The 2 runs with raw bitumen at 360 and 380°C showed a similar trend. A higher temperature (380°C) resulted in an increased TAN reduction rate than a lower temperature (360°C). No significant differences in TAN reduction rate were observed between the two feeds. Soaking temperature played the major role in TAN reduction.

The TAN reduction kinetics was analyzed with the data obtained with the 15 vol% SCO feed. It was found that the TAN reduction followed zero order kinetics with the following kinetic parameters

$$[TAN] = [TAN]_0 - k t \quad \text{Eq. 1}$$

$$k = k_0 e^{(-E_a/RT)} \quad \text{Eq. 2}$$

Activation Energy $E_a = 176.25 \text{ kJ/mol}$

Pre-exponential factor $k_0 = 1.3 \times 10^{12} \text{ mg KOH/g.s}$

Figure 3 shows the zero order kinetics plots with experimental data points. TAN linearly decreased with time. At 360, 375 and 390°C, an acceptable agreement between the model and data was observed. At 380°C, there was a larger deviation between the model and data: the kinetic model predicted a lower TAN reduction than that obtained from the experiment. One of the possible reasons for the deviations could be experimental error in TAN measurement. Note that the TAN value of the feed was 2.26 mg KOH/g while those of the first samples collected during the experiments ranged from 2.26 to 2.35 mg KOH/g (no changes in TAN value was expected for the first samples taken at temperature of 350°C). Nevertheless this zero-order kinetic model provided an approximate TAN reduction behavior of SCO hydrogen donor assisted visbreaking.

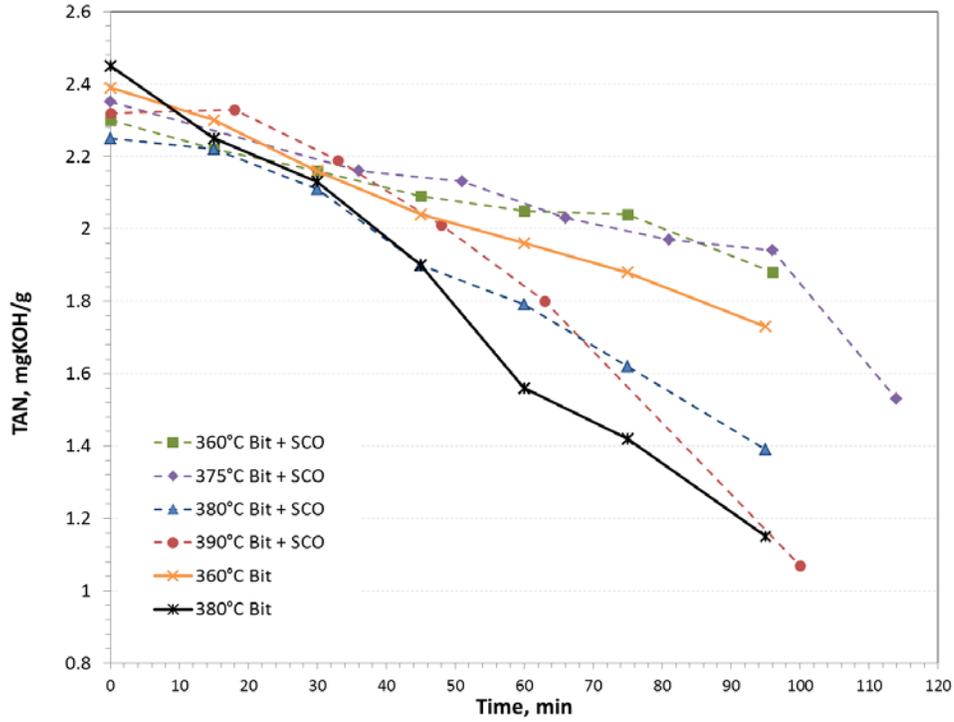


Figure 2 – TAN reduction with time for the 15 vol% SCO feed and raw bitumen feed

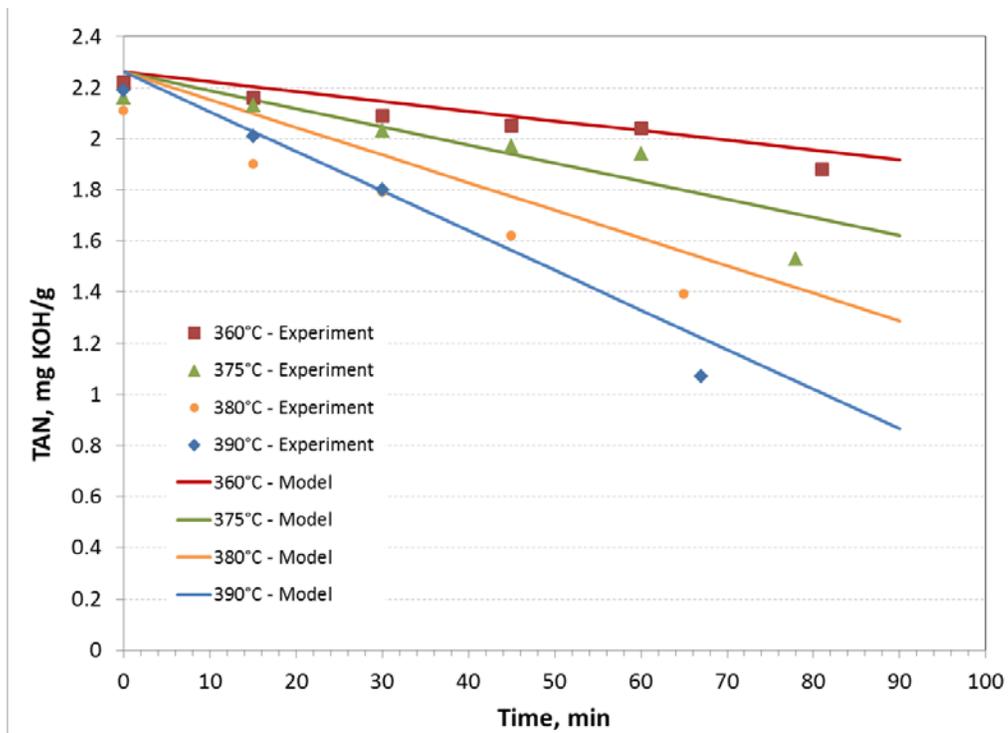


Figure 3 – TAN reduction kinetics: experimental TAN values vs. model prediction

TAN in an oil fraction is mainly contributed by naphthenic acids. The reduction in TAN with time at different temperatures can be explained by the destruction of the naphthenic acid compounds through decarboxylation reactions. Naphthenic acids undergo thermal or catalytic reactions to lose a carboxylic acid group (decarboxylation), producing carbon dioxide (CO₂) and the corresponding hydrocarbon. The CO₂ generated can be a measure of the number of carboxylic acid groups that decomposed, assuming anaerobic conditions: the more CO₂ generated, the greater the reduction in naphthenic acid concentration, assuming the O₂ (oxygen gas) content in the feed is near zero, leading to reduced TAN. Gas produced from the TAN reduction experiments was collected in a gas bag and analyzed by GC. The CO₂ yield was then calculated based on the feed (g CO₂/g Feed). Figure 4 shows the CO₂ yields of the 6 TAN reduction runs, as well as the corresponding TAN reduction. There was a clear correlation between TAN reduction and CO₂ yield. For the 4 runs with the 15 vol% SCO feed the increase in TAN reduction with increased soaking temperature is accompanied by an increase of CO₂ in the produced gas. Note that at 380°C, CO₂ yield was lower than expected. This run had a lower total gas yield compared to the other runs, which might have been due to a gas leak during gas collection.

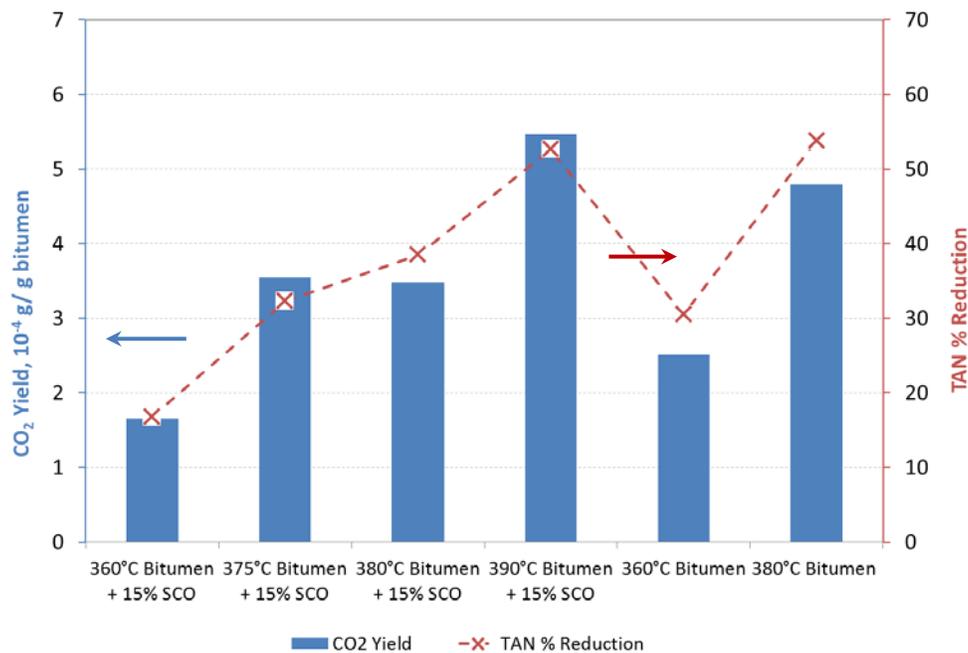


Figure 4 – Carbon dioxide yield with corresponding TAN reduction

4.2.2. EFFECT OF HYDROGEN DONOR SOLVENTS ON VISBREAKING

There have been a number of published studies on the effects of hydrogen donor solvents on visbreaking. The conclusions have been inconsistent. To investigate whether hydrogen donor solvents have any impact on visbreaking, two experiments were conducted with PP8. The feed containing 15-vol% SCO was mixed with two solvents having different H-donor capabilities: a) tetralin, a strong H-donor solvent, and b) naphthalene, a limited H-donor solvent. The feed-to-solvent ratio was 10:1 by weight. Samples were collected at 350, 380, and 415°C, as well as at 10 and 20 min after the autoclave reached 415°C. The autoclave was quenched and the reaction stopped 30 min after the autoclave reached 415°C. Samples collected 20 min after reaching 415°C were analyzed for SARA (saturates-aromatics-resins-asphaltenes) and olefin content by NMR. The results are presented in Table 7. It is seen in Table 7 that there were no substantial differences in the results between the two H-donor solvents. Tetralin as an H-donor would have been expected to have performed better. The reason for this observed similarity in the two runs might be the presence of SCO in the feed, which already provided sufficient hydrogen donation in both runs. If the available transferrable hydrogen in SCO were sufficient for the hydrogen exchange under the reaction conditions, the presence of tetralin or naphthalene would not have a significant effect.

Table 7 – Olefin and SARA analysis results of visbreaking products with tetralin and naphthalene as H-donor

	Tetralin Run	Naphthalene Run
Olefin (wt% 1-decene by NMR)	1.59	1.38
SARA (wt%)		
Saturates	24.42	22.75
Aromatics	35.54	37.17
Polars	14.77	12.81
Asphaltene	12.84	14.88
Light end loss	8.24	6.08
Other Loss	4.20	6.31

4.2.3. EFFECT OF SOAKING, SCO ADDITION AND TEMPERATURE ON VISBREAKING

A set of experiments was conducted with PP8 to investigate the effect of soaking, visbreaking temperature, and SCO addition on the final total liquid products of the visbreaking. A fractional factorial design was used to determine the testing conditions for the experiments. The testing variable and their testing levels are shown in Table 8.

Different feeds were tested to study the effect of SCO addition on the visbreaking products. Experiments with raw bitumen and 15 vol% SCO feed had been completed at the time this report was written. Two more experiments will be conducted using a solvent with minimum hydrogen donation capacity that can simulate the dilution effect of SCO without hydrogen contribution.

The effect of soaking period was initially tested at two levels, no soaking and 40 min soaking. An additional experiment at 20 min soaking was added for the 15 vol% SCO feed. A reaction temperature of 413°C was used in 5 of the 6 experiments, while the sixth was conducted at 400°C with raw bitumen feed without soaking. In all 6 runs the visbreaking reaction time was 15 min. As discovered in previous autoclave experiments, the coking onset limit of this feed was 415°C. Therefore, the visbreaking temperature of 413°C was chosen to achieve the desired level of conversion for reduction of density and viscosity to meet the pipeline specifications. Coke formation was still insignificant. Higher reaction temperatures (>413°C) were not tested while a lower reaction temperature of 400°C was tested in one experiment to check the variation of the liquid product properties at different reaction severities. All 6 runs were conducted at 380°C soaking temperature. Table 9 shows the operating conditions for the experiments, and Figure 5 shows the temperature history of the autoclave reactor from the start to the end of the experiments.

Table 8 – Variables and their levels of the experimental design of the autoclave experiments

Variable	Levels
Visbreaking time (min)	15
Soaking temperature (°C)	380
Soaking time (min)	0, 40
Visbreaking temperature (°C)	400, 413
Bitumen/SCO blending ratio (vol%)	100/0, 85/15

After the autoclave tests were completed, the gas and liquid products were collected. Gas analyses was performed and the liquid products analyzed for density, P value, viscosity, n-C5 insolubles (asphaltene content), toluene insolubles, olefin content by NMR, sulphur, TAN, and SimDis. The 525°C+ fraction conversion was calculated based on the 525°C+ fractional contents in feed and liquid product from the simulated distillation data:

$$\text{Conversion (525°C+)} = \frac{\text{Mass of 525°C+ in Feed} - \text{Mass of 525°C+ in Liquid Product}}{\text{Mass of 525°C+ in Feed}} \quad \text{Eq. 3}$$

Severity index (SI) of the reaction was defined and calculated with the following equation:

$$SI = t e^{\left[-\left(\frac{Ea}{R}\right)\left(\frac{1}{T} - \frac{1}{700}\right)\right]} \quad \text{Eq. 4}$$

Where t = reaction time, in seconds; Ea = activation energy, taken as 50.1 kcal/mole; R = gas constant, 0.001987 kcal/mol.K; T = reaction temperature, K

Mass balances of the autoclave experiments ranged from 97.20% to 99.69%, with an average of 98.14% and a standard deviation of 0.85%. Table 10 summarizes the six runs, their conditions, 525°C+ conversion, and the tests results.

Table 9 – Detailed operating conditions to study the effects of soaking, SCO addition and visbreaking reaction temperature

Run	Conditions			Note
	Feed	Soaking	Reaction	
1	Bitumen	No soaking	413°C, 15 min	Completed
2	Bitumen	No soaking	400°C, 15 min	Completed
3	Bitumen	380 C, 40 min	413°C, 15 min	Completed
4	Bitumen + SCO	No soaking	413°C, 15 min	Completed
5	Bitumen + SCO	380 C, 40 min	413°C, 15 min	Completed
6	Bitumen + SCO	380 C, 20 min	413°C, 15 min	Completed. Additional level of soaking time

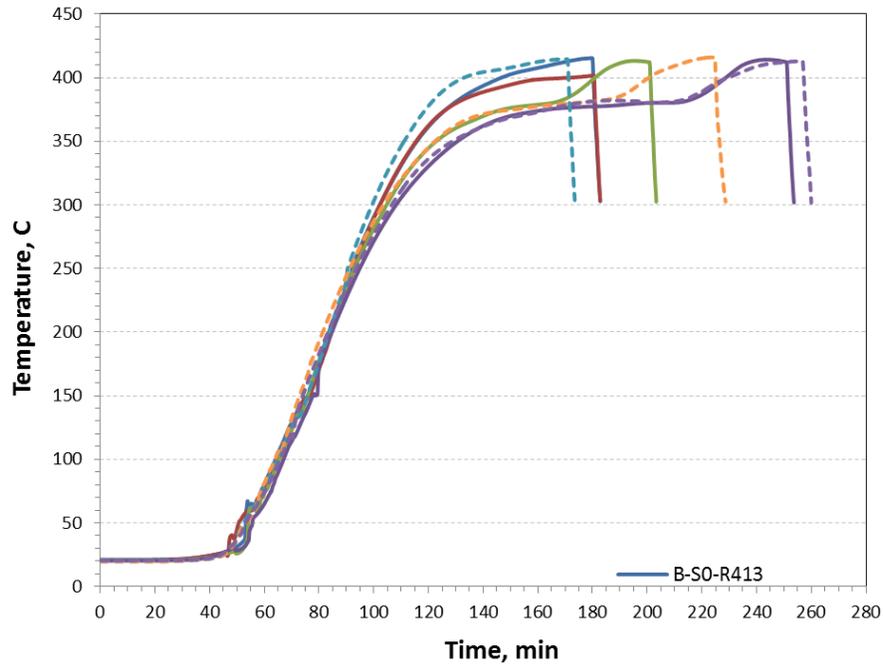


Figure 5 – Temperature history of experiments to study the effects of soaking period and SCO addition on visbreaking

Table 10 – Autoclave test results to study the effects of soaking, SCO additions and visbreaking reaction temperature

Feed	Bitumen				85/15 Bitumen/SCO			
Run Code	Feed	B-S0-R413	B-S0-R400	B-S40-R413	Feed	BSCO-S0-R413	BSCO-S20-R413	BSCO-S40-R413
Conditions		No soaking	No soaking	380°C - 40 min		No soaking	380C – 20 min	380C-40 min
		413°C - 15 min	400°C - 15 min	413°C - 15 min		413°C - 15 min	413°C - 15 min	413°C-15 min
Conversion		34	22	30		37	35	35
SI		915	530	895		960	880	990
P-Value	2.82	Self-incompatible.	1.38	Self-incompatible.		Self-incompatible.	Self-incompatible.	Self-incompatible.
Density (g/ml)	1.0146	0.9905	0.9953	0.9873	0.9928	0.9679	0.9708	0.9672
API (°)	8.0	11.4	10.7	11.8	11.0	14.7	14.3	14.8
Viscosity (cSt at 7°C)	600 (at 80°C)	1506	4264	1655	547 (at 60°C)	326	491	297
C5 insolubles (wt%)	19.64	16.8	16.38	17.45		13.03	13.16	12.72
Toluene insolubles (wt%)	0.01	2.88	0.03	3.35	0.04	3.29	2.23	3.47
Olefin by NMR (wt%)		2.02	1.69	2.55		2.15	2.27	2.11
Sulphur (wt%)	4.74	4.43	4.52	4.38	4.24	3.63	3.77	3.81
TAN (mgKOH/g)	2.49	0.89	1.16	0.71	2.28	0.92	0.88	0.81
MCR (wt%)	14.35	17.72	16.39	17.90	12.04	16.15	14.74	16.06
Mass balance, %		97	100	98		98	98	98

- Raw Bitumen Feed

A raw bitumen feed was tested in three runs: 413°C reaction temperature without soaking (B-S0-R413), 400°C reaction temperature without soaking (B-S0-R400), and 413°C reaction temperature with soaking at 380°C for 40 min (B-S40-R413). As expected, a lower reaction temperature of 400°C resulted in lower conversion of the 525°C+ fraction at 22%, while higher reaction temperature of 413°C resulted in higher conversion of 34% for the run with soaking (B-S0-R413) and of 30% for the run with soaking for 40 min (B-S40-R413).

The two runs conducted at 413°C generated liquid products with comparable densities, which were slightly lower than that of the product generated at 400°C, while the viscosities of the two liquid products obtained at 413°C, 1506 cSt for B-S0-R413 and 1655 cSt for B-S40-R413 at 7°C, were significantly lower than that of the product obtained at 400°C, 4264 cSt for B-S0-R400. This clearly shows that higher temperature resulted in higher visbreaking conversion to thermally crack large hydrocarbon molecules into small ones. However, the two products obtained at 413°C had significantly higher TI material, 2.88wt% for B-S0-R413 and 3.35wt% for B-S40-R413, compared to that obtained at 400°C, 0.03wt% for B-S0-R400. This observation indicates that certain degree of coking occurred at 413°C, and that soaking slightly increased the coke formation. Note that the two products obtained at 413°C were self-incompatible with indeterminable P-value, meaning that they were unstable and asphaltenes tended to precipitate without adding any solvents. Note that the severity indices of these two products were around 900, much higher than 800, a commonly accepted severity index at which coking starts (coking onset). The product obtained at 400°C (B-S0-R400) had a P-value of 1.38, representing reasonable stability.

Olefin content in the liquid products varied among the three runs. The run conducted at 400°C generated the lowest olefin content in the liquid product of 1.69wt%. The other two runs conducted at 413°C generated higher olefin contents of 2.02wt% for the one without soaking and 2.55wt% for the one with soaking for 40 minutes. Again, it can be concluded that soaking improved visbreaking conversion and therefore, increased olefin formation, which is not desired.

All the 3 runs with raw bitumen as feed showed significant reductions in TAN value from that of the feed (2.49 mg KOH/g). The TAN reduction was the least in the case of 400°C. Both the 2 runs at 413°C showed higher TAN reduction than that at 400°C. The run with soaking resulted in a product TAN value of 0.71 mg KOH/g while the one without soaking resulted in a product TAN

value of 0.89 mg KOH/g. Once more, these observations indicate that high temperature and soaking improved visbreaking conversion and TAN reduction.

There was a slight reduction in sulphur content as seen in Table 10. The run at 400°C generated a product with sulphur content of 4.52 wt%, which the two runs at 413°C generated products with sulphur content of 4.38 wt% for the one with soaking and 4.43 wt% for the one without soaking. Both high temperature and soaking played a minor but positive role in sulphur reduction.

The general observation is that higher reaction temperature resulted in higher visbreaking conversion of the 525°C+ material, which had a significant impact on reducing the liquid product viscosity, formation of toluene insoluble material and olefins, and in reducing TAN value. The impacts of soaking were also noticeable, but not as significant as reaction temperature.

Gas analysis by GC was performed to determine light hydrocarbon composition (Table 11). The yield of each gas component was then calculated based on the GC analysis results and the total amount of gas collected during the run, represented as g/g Feed as shown in Table 12. For the 3 runs with raw bitumen as the feed, there were significant differences in gas yields between different temperatures. Between the 2 runs at 413°C, the one with soaking had slightly lower yields for most of the gas components and for the overall gas yield, indicating that soaking slightly reduced gas formation. The yields of light hydrocarbons (alkanes and alkenes) of C1 to C5 at 413°C were consistently higher than those at 400°C, which was due to the higher thermal cracking severity and conversion at high temperature. The yields of H₂, carbon monoxide (CO), and CO₂ were also consistent with thermal cracking severity and conversion. The higher the thermal cracking severity and conversion, the higher the yield of H₂, CO and CO₂. However, the yields of hexanes showed a different trend - the hexanes yield at 413°C were lower than that at 400°C, while between the 2 runs at 413°C, the one with soaking had an even lower hexane yield than the one without soaking. This could be caused by secondary thermal cracking of hexanes at higher temperature and with soaking. The trends of hydrogen sulphide yields were consistent with those of light hydrocarbons and consistent with the sulphur reduction in the liquid products as discussed above. Carbonyl sulphide was detected in much lower amounts compared to hydrogen sulphide. The yield of carbonyl sulphide also followed the trend of light hydrocarbons.

Table 11 – Gas composition from GC analysis (raw bitumen feed)

Component	Gas composition (vol%)		
	B-S0-R413	B-S0-R400	B-S40-R413
Hydrogen	6.5514	7.8117	7.8947
Oxygen	0.0000	0.0000	0.0000
Methane	47.2745	44.1776	46.0526
Carbon monoxide	1.7825	2.0136	1.5469
Carbon dioxide	3.0531	3.9301	3.4673
Ethylene	0.2381	0.2669	0.2134
Ethane	12.7421	11.5478	12.7845
Acetylene	0.0000	0.0000	0.0000
Hydrogen sulphide	19.3447	22.8530	20.1102
n-Propane	5.9617	4.4396	5.0498
Cyclopropane	0.0000	0.0000	0.0000
Propylene	0.6323	0.4852	0.4267
iso-Butane	0.2719	0.2426	0.2667
n-Butane	1.1195	1.0189	1.1024
t-2-Butene	0.0896	0.0970	0.0889
1-Butene	0.1004	0.0970	0.0889
iso-Butene	0.1496	0.1698	0.1422
c-2-Butene	0.0557	0.0728	0.0711
iso-Pentane	0.2519	0.2669	0.2667
n-Pentane	0.2319	0.2669	0.2667
1,3-Butadiene	0.0000	0.0000	0.0000
3-methyl-1-Butene	0.0000	0.0000	0.0000
t-2-Pentene	0.0000	0.0000	0.0000
2-Methyl-2-Butene	0.0000	0.0000	0.0000
1-Pentene	0.0000	0.0000	0.0000
2-Methyl-1-Butene	0.0000	0.0000	0.0000
c-2-Pentene	0.0000	0.0000	0.0000
Hexanes	0.0791	0.1698	0.0533
Heptanes	0.0282	0.0243	0.0178
Octanes	0.0000	0.0000	0.0000
Nonanes	0.0000	0.0000	0.0000
Carbonyl sulphide	0.0419	0.0485	0.0889
Helium	0.0000	0.0000	0.0000

Table 12 – Gas yields of main components (raw bitumen feed)

Component	Gas yield (x 10 ⁻⁶ g/g Feed)		
	B-S0-R413	B-S0-R400	B-S40-R413
Hydrogen	100.22	69.81	108.95
Methane	5755.26	3141.89	5057.82
Carbon monoxide	378.89	250.03	296.63
Carbon dioxide	1019.63	766.77	1044.64
Ethylene	50.69	33.19	40.98
Ethane	2907.57	1539.35	2631.74
Hydrogen sulphide	5003.05	3452.77	4692.03
n-Propane	1994.95	867.88	1524.43
Propylene	201.93	90.51	122.94
iso-Butane	119.91	62.51	106.13
n-Butane	493.78	262.55	438.66
t-2-Butene	38.16	24.14	34.15
1-Butene	42.73	24.14	34.15
iso-Butene	63.71	42.24	54.64
c-2-Butene	23.71	18.10	27.32
iso-Pentane	137.91	85.36	131.74
n-Pentane	126.94	85.36	131.74
Hexanes	51.72	64.88	31.47
Heptanes	21.42	10.78	12.20
Carbonyl sulphide	19.10	12.92	36.56
Total gas yield	18551.27	10905.16	16558.91

- 85/15 Bitumen/SCO Feed

The 85/15 bitumen/SCO feed used in the PP5 experiments was also tested with 3 runs as shown in Table 10: one at 413°C without soaking (BSCO-S0-R413), two at 413°C with soaking at 380°C for 20 min (BSCO-S20-R413), and for 40 min (BSCO-S40-R413). The 3 runs showed similar visbreaking conversions of 525°C+ material ranging from 35% to 37%. Different soaking periods did not have a significant effect on the visbreaking conversion due to the fact that the severity indices of the 3 runs were close to each other, ranging from 880 to 990.

The densities of the 3 liquid products were comparable and ranged from 0.9672 to 0.9708 g/ml. Significant reductions in liquid product viscosity were observed for all the 3 runs. The run

with soaking for 40 min resulted in the lowest product viscosity of 297 cSt at 7°C, followed by the one without soaking with a product viscosity of 326 cSt. The one with soaking for 20 min resulted in a product viscosity of 491 cSt. These products met or were close to meeting the pipeline specification for viscosity of 350 cSt. The run with soaking for 20 min had the lowest reaction severity among the three runs, which could explain the higher viscosity of the product as compared to the other two. This lower severity index could be due to fluctuations in autoclave temperature control and reaction termination although all 3 runs were set at 413°C for 15 min.

The pentane insolubles (asphaltene content) in the liquid product were not significantly affected by soaking. The three runs showed similar pentane insolubles contents ranging from 12.7 to 13.2 wt%. Toluene insolubles contents of the 3 products were significantly higher compared to the feed (0.04 wt%), indicating a certain degree of coke formation. The run with soaking for 20 min generated a product with the lowest toluene insolubles of 2.23 wt%, followed by the run without soaking which generated a product with toluene insolubles of 3.29 wt%. The run with soaking for 40 min generated a product with toluene insolubles of 3.47 wt%. All three products were self-incompatible, meaning that they were unstable, with a tendency of asphaltene precipitation at room conditions.

The olefin contents of the 3 liquid products were similar, ranging from 2.11 to 2.27 wt%. Soaking did not have a significant effect of olefin formation since the severity indices of the 3 runs were similar and since soaking generated insignificant amounts of olefins due to the low temperature (380°C).

Significant reduction in TAN was also observed for the 3 runs. The highest TAN reduction was observed for the run with soaking for 40 min (0.81 mg KOH/g), followed by the run with soaking for 20 min (0.88 mg KOH/g). The run without soaking had a TAN of 0.92 mg KOH/g. Similar to the trend in TAN reduction for raw bitumen, increased TAN reduction with soaking time was consistent with the TAN reduction kinetics study discussed earlier in this report.

Pronounced sulphur reduction was evident for all the 3 runs, more significant than the 3 runs with the raw bitumen feed, as shown in Table 10.

In summary, soaking did not significantly affect liquid product density, viscosity, pentane insolubles, toluene insolubles or sulphur content. However, increased soaking time resulted in higher TAN reduction, which is consistent with the TAN reduction kinetics.

The gas composition results obtained by GC analysis are shown in Table 13, and the yields of the gas components are presented in Table 14. The total gas yields of the 3 runs were quite close to each other, which is consistent with visbreaking conversion and product properties as discussed above. Among the 3 runs, the one with soaking for 40 min had a higher total gas yield (and most of the individual components) than the other 2 runs, which is different from the trend observed with the raw bitumen feed discussed earlier. On the other hand, the run without soaking had the highest yields of hexanes and heptanes, indicating that soaking resulted in secondary thermal cracking of hexanes and heptanes. This observation is consistent with that made with the raw bitumen feed (Table 12). The yields of hexanes and heptanes were very low compared to other lighter hydrocarbons. The H₂ yields of the 3 runs were almost the same. The yield of CO₂ increased with increasing soaking time while that of CO showed the opposite trend. The combined yields of CO₂ and CO for the 3 runs were almost identical, indicating similar degrees of decarboxylation of naphthenic acids. This observation is consistent with the TAN reduction of the 3 runs, as discussed above. The yields of hydrogen sulphide for the 3 runs were similar, although the run with soaking for 40 min had a slightly higher hydrogen sulphide yield, which was the result of higher visbreaking conversion for this run. No carbonyl sulphide was formed in any of the 3 runs.

- Liquid Product Yields of Individual Fractions

The liquid product yields of individual fractions, naphtha (IBP-200°C), light gas oil (200-343°C), heavy gas oil (343-525°C) and residue (525°C-FBP) were calculated from SimDis data for all the 6 runs, and are shown in Figure 6. In general, higher visbreaking conversion resulted in higher yields of naphtha and heavy gas oil, which is especially evident in the 3 runs conducted with the raw bitumen feed. It is interesting that the yields of light gas oil were similar for a given feed, regardless of the visbreaking conversion. The liquid product yields of individual fractions in the 3 runs with 15 vol% SCO feed were quite similar since they had similar visbreaking conversions.

Table 13 – Gas composition from GC analysis (15 vol% SCO feed)

Component	Gas composition (vol%)		
	BSCO-S0-R413	BSCO-S20-R413	BSCO-S40-R413
Hydrogen	7.8981	8.1123	7.0067
Oxygen	0.0000	0.0000	0.0000
Methane	49.2080	49.0228	49.2718
Carbon monoxide	1.4983	1.3476	0.5468
Carbon dioxide	3.0394	3.2906	3.3466
Ethylene	0.2568	0.2598	0.2441
Ethane	12.9495	12.7237	13.3935
Acetylene	0.0000	0.0000	0.0000
Hydrogen sulphide	17.5514	18.1351	18.1958
n-Propane	4.7731	4.4245	5.0033
Cyclopropane	0.0000	0.0000	0.0000
Propylene	0.4495	0.4549	0.4630
iso-Butane	0.2568	0.2342	0.2868
n-Butane	1.0916	1.0298	1.2283
t-2-Butene	0.0856	0.0928	0.1021
1-Butene	0.0856	0.0908	0.0992
iso-Butene	0.1284	0.1446	0.1442
c-2-Butene	0.0642	0.0578	0.0607
iso-Pentane	0.2568	0.2551	0.2892
n-Pentane	0.2568	0.2525	0.2781
1,3-Butadiene	0.0000	0.0000	0.0000
3-methyl-1-Butene	0.0000	0.0000	0.0000
t-2-Pentene	0.0000	0.0000	0.0000
2-Methyl-2-Butene	0.0000	0.0000	0.0000
1-Pentene	0.0000	0.0000	0.0000
2-Methyl-1-Butene	0.0000	0.0000	0.0000
c-2-Pentene	0.0000	0.0000	0.0000
Hexanes	0.1284	0.0572	0.0398
Heptanes	0.0214	0.0139	0.0000
Octanes	0.0000	0.0000	0.0000
Nonanes	0.0000	0.0000	0.0000
Carbonyl sulphide	0.0000	0.0000	0.0000
Helium	0.0000	0.0000	0.0000

Table 14 – Gas yields of main components (raw bitumen feed)

Component	Gas yield (x 10 ⁻⁶ g/g Feed)		
	BSCO-S0-R413	BSCO-S20-R413	BSCO-S40-R413
Hydrogen	93.51	95.21	92.43
Methane	4636.68	4578.74	5172.91
Carbon monoxide	246.49	219.76	100.23
Carbon dioxide	785.64	843.13	963.84
Ethylene	42.32	42.44	44.82
Ethane	2287.04	2227.47	2635.62
Hydrogen sulphide	3513.32	3598.35	4058.28
n-Propane	1236.23	1135.89	1443.84
Propylene	111.09	111.46	127.50
iso-Butane	87.68	79.25	109.10
n-Butane	372.66	348.47	467.20
t-2-Butene	28.21	30.31	37.48
1-Butene	28.21	29.66	36.44
iso-Butene	42.32	47.23	52.95
c-2-Butene	21.16	18.89	22.29
iso-Pentane	108.85	107.15	136.54
n-Pentane	108.85	106.08	131.30
Hexanes	65.00	28.68	22.46
Heptanes	12.60	8.13	0.00
Carbonyl sulphide	0.00	0.00	0.00
Total gas yield	13828	13656	15655

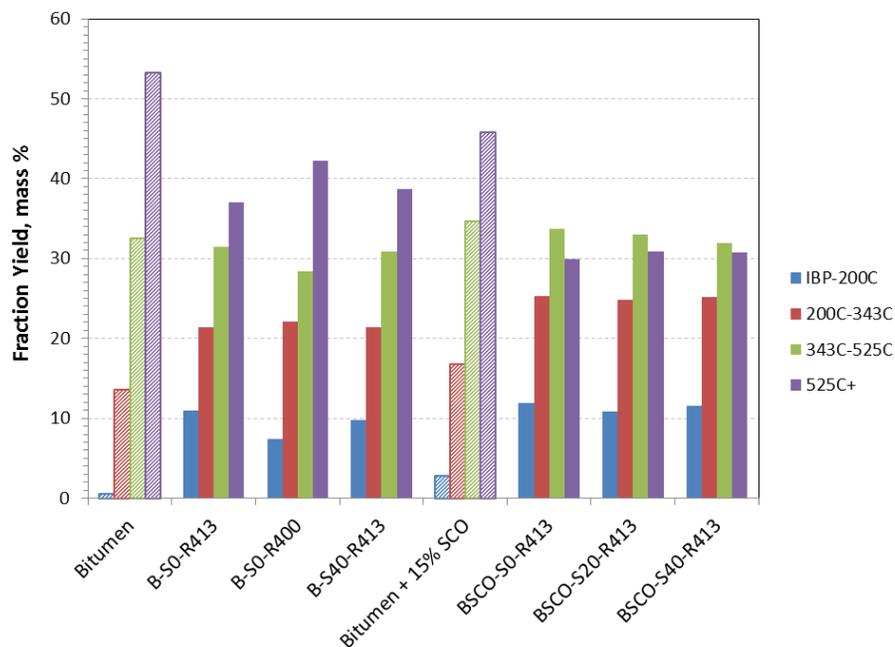


Figure 6 – Fractional yield of liquid products of raw bitumen feed and bitumen + SCO feed and total liquid products

To investigate the dilution effect of SCO versus the role SCO played in soaking and visbreaking, the 2 total liquid products obtained with the raw bitumen feed at 413°C were each blended with 15 vol% SCO (B-S0-R413 + 15 vol% SCO and B-S40-R413 + 15 vol% SCO). These blends were analyzed for the various properties listed in Table 10. The results were further compared with those obtained with the 15 vol% SCO feed (BSCO-S0-R413 and BSCO-S40-R413). Table 15 shows the comparisons. It is seen that the dilution effect of SCO after raw bitumen visbreaking is evident, effectively reducing density, viscosity, C5 insolubles, toluene insolubles, olefin and sulphur contents, and TAN values. The addition of SCO to the visbreaking products (B-S0-R413 + 15 vol% SCO and B-S40-R413 + 15 vol% SCO) did not change their stability (or P-value). The addition of SCO into bitumen before visbreaking (BSCO-S0-R413 and BSCO-S40-R413) promoted thermal cracking, resulting in much lower product viscosity than that obtained by simply blending of SCO with raw bitumen visbreaking products (B-S0-R413 + 15 vol% SCO and B-S40-R413 + 15 vol% SCO). The impacts of SCO on other properties (additional to dilution effect) were not evident in Table 15. Note that this comparison was based on a single visbreaking temperature with one bitumen/SCO ratio. To reach a more reliable conclusion a more systematic study should be conducted by varying visbreaking

temperature and soaking temperature, bitumen/SCO blending ratio, and other operating parameters.

Table 15 – Comparison of liquid properties for SCO addition before and after visbreaking

Sample	No soaking		Soaking for 40 min	
	B-S0-R413 + 15 vol% SCO	BSCO-S0- R413	B-S40-R413 + 15 vol% SCO	BSCO-S40- R413
P-Value	Self- incompatible	Self- incompatible	Self- incompatible	Self- incompatible
Density (g/ml)	0.9729	0.9679	0.9705	0.9672
API (°)	13.9	14.7	14.3	14.8
Viscosity (cSt at 7°C)	566.54	326.12	747.99	297.42
C5 insolubles (wt%)	13.99	13.03	14.42	12.72
Toluene insolubles (wt%)	2.87	3.29	3.25	3.47
Olefin by NMR (wt%)	1.67	2.15	1.65	2.11
Sulphur (wt%)	3.76	3.63	3.74	3.81
TAN (mgKOH/g)	0.67	0.92	0.62	0.81
MCR (wt%)	TBA	TBA	TBA	TBA

5.0 CONCLUSIONS

Extensive pilot plant tests have been conducted to study and demonstrate the H-donor assisted visbreaking of Canadian bitumen with synthetic crude oil (SCO) as the hydrogen donor. Various lab tests were performed with the feedstocks and products obtained from these pilot plant runs. The results of the pilot plant tests with PP5 and PP8 are summarized separately as follows.

PP5 continuous pilot plant tests:

1. Four commissioning runs and 32 experimental runs were completed with CanmetENERGY's PP5 pilot plant. Some operational issues (pressure buildup, coke formation, breaking of mixer shaft, etc.) occurred and were resolved without significantly delaying the project. The concept of hydrogen donor assisted visbreaking by using SCO was tested under different operating conditions and with feedstocks having different bitumen/SCO ratios. All the runs had reasonable mass balances of 100±5%.

2. The visbreaking products from PP5 pilot plant tests were analyzed.
3. The repeatability of PP5 pilot plant runs and the consistency of pilot plant and lab test data were validated by conducting 4 replicate runs. Mass balance and analytical results of both soaking and visbreaking product were relatively constant and within the experimental error ranges.
4. Under the studied operating conditions and with either 5 or 12.5 vol% SCO feedstock, the visbreaking products did not meet the desired viscosity and density pipeline specifications of 350 cSt (at 7°C) and 19° API gravity, respectively. With the 15 and 20 vol% SCO feedstocks, the viscosities of the visbreaking products were as low as 872 and 861 cSt (± 56 cSt), quite close to the target of 350 cSt, while the API gravities of these products were around 14° ($\pm 0.1^\circ$).
5. Blending 5 wt% n-pentane into the visbreaking products obtained with 15 and 20 vol% SCO feedstocks could easily give the viscosity target of 350 cSt in most cases.
6. The visbreaking products had a TAN in the range of 1.0 to 1.7 mg KOH/g (± 0.02 mg KOH/g), which represents a significant reduction from that of the feedstocks (1.99 to 2.32 mg KOH/g). Their olefin contents were in the range of 1.0 to 2.3 wt% (± 0.03 wt%), depending on visbreaking severity. The stabilities of the visbreaking products were reasonable with P-values 0 (by Wiehe's method) in the range of 1.2 to 2. Sulphur contents were slightly decreased to about 3.68 to 4.46 wt% (± 0.03 wt%) from that of the feeds (3.98 ~ 4.50 wt%).
7. The naphtha fraction obtained from distilling the visbreaking product had a high olefin content of 10 to 12 wt%, which is understandable since most of the olefins formed during visbreaking were small molecules in the naphtha boiling range. The light gas oil fraction also had significant olefin content of 2.5 to 2.8 wt%, whereas the residue fraction had an olefin content of 0.6 to 0.9 wt%. The light gasoil fraction had lower TAN of 0.6 to 0.9 mg KOH/g, whereas the naphtha and the residue fractions had higher TAN of 1.1 to 2.4 mg KOH/g, respectively.
8. In the naphtha fraction, there were significant amounts of sulphides, mercaptans and thiophenes. In the total liquid product there were benzothiophene and its derivatives. The majority of the sulphur species could not be identified.

9. Given similar operating conditions, longer residence times resulted in higher visbreaking and decarboxylation reaction conversions, and therefore lower TAN (and higher product value). However the products were less stable (lower P-Value). Thus there was a trade-off between TAN reduction and product stability.
10. Higher pressure could help reduce olefin formation, and to less extent, increase visbreaking conversion.

PP8 batch autoclave tests:

1. Three sets of experiments were conducted in the batch autoclave reactor (PP8) to study: a) TAN reduction kinetics, b) effect of different H-donor solvents, and c) effects of different soaking conditions, reaction temperature and SCO addition on liquid products properties. The batch autoclave was modified to accommodate inline sample collection of the reaction liquid to study TAN reduction kinetics.
2. Six runs were conducted to study the TAN reduction kinetics during soaking with two different feedstocks: 4 runs with an 85/15 (vol/vol) bitumen/SCO feedstock and 2 runs with a raw bitumen feedstock. The experiments were conducted at soaking temperatures ranging from 360 to 390°C. Both feeds had similar trends of increased TAN reduction with increase in soaking time. Higher soaking temperatures (380 and 390°C) resulted in higher TAN reduction rate than lower soaking temperatures (360 and 375°C) regardless of the feed used.
3. TAN reduction kinetics for the 85/15 bitumen/SCO feed followed zero order kinetics, with activation energy of 176.25 kJ/mol and pre-exponential factor of 1.3×10^{12} mg KOH/g. The TAN reduction in liquid product was consistent with CO and CO₂ yields in the gaseous product and can be explained by the extent of decarboxylation reaction of naphthenic acids.
4. Adding two different H-donor solvents of different hydrogen donation capabilities, tetralin and naphthalene, to the 85/15 bitumen/SCO feed did not have a significant impact on SARA compositions or olefin contents of the liquid products. However, these tests were inconclusive since the presence of SCO as a hydrogen donor in the feed might have provided the required hydrogen donation capacity.

5. Six runs were conducted to study the effect of soaking, reaction temperature and SCO addition on visbreaking liquid products. Three runs were conducted with the raw bitumen feed and the other three were conducted with the 85/15 bitumen/SCO feed. For the raw bitumen feed, a higher visbreaking temperature (413°C) resulted in significantly lower product viscosity and TAN value, but higher toluene insolubles (indication of coke formation), due to higher extents of thermal cracking and decarboxylation of naphthenic acids. The impact of soaking was not as significant as that of temperature. Higher temperature also resulted in higher total gas yield and higher yields of hydrogen, CO and CO₂, light hydrocarbons, and hydrogen sulphide.
6. The 3 runs with the 85/15 bitumen/SCO feed were conducted at the same reaction temperature of 413°C and different soaking times. Increasing soaking time did not increase visbreaking conversion, but slightly improved the properties of the liquid products. The notable improvements in properties were viscosity and TAN that were achieved at the longest soaking time (40 min). Sulphur conversion was similar among the 3 runs, but higher than those achieved with the raw bitumen feed. The total gas yields among the 3 runs were comparable as they had similar visbreaking conversions.
7. Higher visbreaking conversion resulted in higher yields of naphtha and heavy gas oil. Light gas oil yield remained relatively constant.

While blending SCO directly with the liquid products obtained with the raw bitumen feed showed an evident effect of dilution on the liquid properties, adding SCO as hydrogen donor into raw bitumen as feed for visbreaking resulted in a significant reduction in viscosity compared to the direct blending of SCO with the visbreaking product of raw bitumen obtained at the same operating conditions. The use of SCO as hydrogen donor promoted visbreaking in addition to the dilution effect.

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APPENDIX A: SIMDIS DATA OF FEEDSTOCKS AND PRODUCTS

SIMDIS DATA OF FEEDSTOCKS AND PRODUCTS

Sample ID	Bitumen	SCO	85/15 bitumen/SC O feed	1-S	1-HS	1-TLP	2-HS	2-TLP	3-HS	85/15 bitumen/SC O feed	4-S	4-HS
Mass %	BP	BP	BP	BP	BP	BP	BP	BP	BP	BP	BP	BP
0.5	190.6	0	109.4	105.8	48.4	36	46.8		36	42.4	102.8	53.4
1	209.6	36	160.8	146	83.8	38.2	82	36	80.8	128.8	151.6	88.2
2	231.6	59.4	199	191	118.4	99.4	112.8	77	105.2	185.6	195.8	127.8
3	248.8	95.2	216.6	211.8	142.2	128.2	135.4	107.8	126.8	211.6	217.2	155.2
4	261.8	116.4	230.4	226.2	161.2	148.8	153.4	132	141	227.8	232	175
5	273.2	134.2	242.8	239.2	177.2	166.2	167.4	149.2	157.2	241.6	245.2	193.6
6	283.8	148.2	253	249.8	191.2	181	180	163	172	253.4	256.2	207.2
7	293	163.4	262.2	259.4	202.2	194.4	191.6	177.2	185.4	263	265.6	218.6
8	301.2	174.4	270.8	268.2	211.8	205	201.4	190.2	196.4	271.8	274.4	228.4
9	308.8	187.4	278.8	276.4	220	214	210.4	200	205.4	280.4	282.6	237.8
10	316.2	197.8	286.2	284	227.8	222	217.6	209.2	213.2	288.2	290.2	246.6
11	323.4	208.4	292.6	290.6	235.4	230	224.6	216.6	220.2	295.2	297	254.6
12	330.4	216.8	298.8	297	242.4	237.6	231.6	223.8	227.4	301.8	303.4	261.8
13	337	225	304.8	303	249	244.4	238.6	231	234.2	307.8	309.4	268.8
14	343.8	231.6	310.4	308.8	255.8	251.2	244.6	238	240.2	313.6	315.2	275.4
15	350	237.6	315.8	314	261.8	257.8	251	244.4	246.6	319.2	321	282.2
16	356.2	243.6	321.4	319.6	267.8	263.8	257	250.8	252.8	325	326.8	288.6
17	362.4	249.2	326.8	325.2	273.8	269.6	262.6	257	258.4	330.6	332.4	294.2
18	368.4	254.2	332.4	330.6	279.6	275.6	268.2	262.6	264.2	336.2	337.8	299.8
19	374.4	258.4	337.8	336	285.2	281.4	273.8	268.2	269.6	341.8	343.6	305.2
20	380.6	263.2	343.2	341.4	290.2	287	279.2	274	275.2	347	348.8	310.2
21	386.8	267.2	348.4	346.6	295.2	292	284.6	279.6	280.6	352.2	354	315.4
22	392.8	271.2	353.4	351.8	300.2	297	289.4	285	285.4	357.2	359.2	320.4
23	398.8	274.8	358.6	356.8	304.8	302	294.2	289.8	290.4	362.6	364.4	325.4
24	404.8	279.2	363.6	361.8	309.6	306.6	299	294.8	295.2	367.8	369.6	330.4
25	410.4	282.8	368.8	367	313.8	311.2	303.6	299.6	300	372.8	374.8	335.2
26	416	286.6	374	372	318.4	315.6	308.2	304.2	304.6	378	380.2	340.4
27	421.4	289.6	379.2	377.4	323.2	320.2	312.4	308.8	308.8	383.4	385.6	345.2
28	426.6	293.4	384.6	382.6	327.6	325	316.6	313	313.4	388.6	391	350
29	432	296.6	389.8	387.8	332.2	329.6	321.4	317.6	318	393.8	396.4	354.8
30	437	299.8	395	393	337	334.2	325.8	322.4	322.6	399.2	401.6	359.4
31	442.4	302.6	400.2	398.2	341.6	338.8	330.2	326.8	327.2	404.4	407	364
32	447.8	305	405.2	403.2	346.2	343.6	334.8	331.2	332	409.4	412	368.8
33	453.2	307.8	410.2	408.2	350.4	348	339.4	336	336.8	414.4	417.2	373.6
34	459	310.6	415	413	354.8	352.4	344	340.6	341.4	419.4	422.2	378.4
35	464.6	313	419.8	417.8	359.4	356.8	348.2	345.2	346	424.2	427.2	383.2
36	470.2	315.8	424.8	422.6	363.8	361.4	352.4	349.6	350.6	429	432.2	388.2
37	476	318.2	429.6	427.6	368.2	365.8	356.8	353.8	355	434	437.2	393.2
38	481.4	320.6	434.6	432.4	372.8	370.4	361.2	358.4	359.6	438.8	442.4	398.2
39	487	323.4	439.6	437.4	377.6	375	365.6	362.8	364.4	443.8	447.6	403
40	492.4	326	445	442.6	382.2	379.8	370	367.2	369.2	448.8	453.2	408

Sample ID	Bitumen	SCO	85/15 bitumen/SC O feed	1-S	1-HS	1-TLP	2-HS	2-TLP	3-HS	85/15 bitumen/SC O feed	4-S	4-HS
Mass %	BP	BP	BP	BP	BP	BP	BP	BP	BP	BP	BP	BP
41	497.6	328.8	450.6	448	387	384.6	374.6	371.8	374	454	458.8	412.8
42	502.8	331.2	456.2	453.6	391.8	389.4	379.2	376.6	379	459.4	464.6	417.6
43	507.6	333.4	462	459.2	396.4	394.2	384	381.4	384	464.8	470.2	422.4
44	512.4	336.2	468	465.2	401.2	399	388.6	386	389	470.2	476	427.2
45	517	338.6	473.8	471	405.8	403.6	393.4	391	394	475.4	481.8	432
46	521.6	341.2	479.6	476.6	410.6	408.4	398	395.8	399	480.6	487.6	437
47	526.2	343.8	485.4	482.6	415.2	413.2	402.8	400.4	404	485.8	493.4	442
48	530.6	346	491.4	488.4	419.8	417.8	407.4	405.2	409	491	499	447.2
49	535.2	348.6	497.2	494.4	424.6	422.6	412.2	410	414.2	496	504.4	452.6
50	540	351	503	500.2	429.6	427.4	416.8	414.8	419.4	500.8	509.8	458.2
51	545	353.4	508.6	506	434.6	432.4	421.6	419.6	424.6	505.4	515.2	464
52	550	356	514	511.6	439.6	437.6	426.4	424.6	430.2	510	520.6	469.6
53	555.2	358.2	519.4	517.2	445	442.8	431.4	429.6	436	514.6	525.8	475.4
54	560.4	360.8	524.8	522.6	450.4	448.2	436.6	434.8	441.8	519	531.2	481.2
55	565.6	363.4	529.8	528	456.2	454	441.8	440	448	523.4	537	487.2
56	571	365.8	535	533.2	462	459.8	447.2	445.6	454.4	527.8	543	493.2
57	576.4	368.4	540	538.6	468	465.8	452.8	451.2	461	532.4	549.2	499.2
58	581.6	370.8	545.6	544	473.8	471.6	458.6	457.2	467.6	537.4	555.6	505.2
59	586.8	373.4	551.4	549.8	479.8	477.6	464.6	463.2	474	542.4	562.2	511.2
60	592.2	375.8	557.2	555.8	486	483.8	470.6	469.4	480.8	547.6	568.8	517.4
61	597.6	378.4	563.2	561.8	492.2	490.2	476.6	475.4	487.6	553	575.6	523.4
62	603	381	569.2	568	498.6	496.6	482.8	481.8	494.8	558.4	582.2	529.6
63	608.6	383.6	575.4	574.2	505	503	489	488.2	501.8	563.8	589	536.2
64	614	386.2	581.6	580.4	511.4	509.4	495.4	494.8	508.8	569.4	596	543
65	619.4	388.8	587.8	586.8	518	516	501.8	501.4	516	575	603	550
66	624.8	391.6	594.2	593.2	524.6	522.8	508.4	508.2	523.2	580.6	610	557
67	630.4	394.2	600.6	599.8	531.2	529.4	515	515	530.6	586.2	617	564
68	635.8	397	607	606.2	538	536.2	521.8	522	538.2	591.8	624	571.2
69	641.4	399.8	613.4	612.8	545	543.2	528.6	528.8	546.2	597.4	631	578.4
70	646.8	402.6	619.8	619.4	552.4	550.6	535.4	536	554.8	603.2	638.2	585.6
71	652.6	405.4	626.2	625.8	560	558.2	542.6	543.4	563.6	608.8	645.4	593.2
72	658.2	408.2	632.6	632.4	567.4	565.8	550.2	551.2	572.6	614.6	652.6	600.8
73	664	411.2	639	639	575.2	573.6	557.8	559.2	581.8	620.2	660	608.4
74	670	414	645.6	645.8	583.2	581.6	565.6	567.2	591.4	625.8	667.6	616.2
75	676.2	417	651	651.4	591.4	589.8	573.6	575.6	601.4	631.6	675.2	624.2
76	682.4	420.2	656.2	656.6	600	598.2	581.8	584	611.6	637.4	682.8	632.4
77	688.8	423	661.4	662.2	608.8	607	590.2	593	622.2	643.2	690.6	640.8
78	694.8	426.2	668.4	669.8	617.6	616	599.2	602	633	649	698.6	649.6
79	700.8	429.2	677	678.8	626.6	624.8	608.2	611.4	644.6	654.8	706.8	658.6
80	706.2	432.4	685.8	687.8	636	634.2	617.4	621	654.6	660.8	715.4	668.2
81	712	435.6	694.8	697	645.8	644	626.8	630.8	665.2	666.8	724.4	678.2
82	718.6	438.8	703.8	706.6	654	652.6	636.6	641.2	682.8	673	734.4	688.6
83	725.8	442	713.4	716.4	662.2	660.8	646.8	650.8	701.8	679.2	745.8	699.6
84	733.2	445.4	723.6	726.6	675.4	673	655.4	659.8	723	685.6	750	711.2

Sample ID	Bitumen	SCO	85/15 bitumen/SC O feed	1-S	1-HS	1-TLP	2-HS	2-TLP	3-HS	85/15 bitumen/SC O feed	4-S	4-HS
Mass %	BP	BP	BP	BP	BP	BP	BP	BP	BP	BP	BP	BP
85	750	449	734.6	737.8	690.4	688.2	664.6	672.4	747.4	692		724.2
86		452.6	747.2	750	706.8	704.8	680	689	750	698.8		739
87		456.4	750		724.8	723.2	696.8	707.4		705.6		750
88		460.2			746.4	745.8	715.4	728.6		712.8		
89		464.4			750	750	737.2	750		720.2		
90		468.8					750			728.2		
91		473.6								737.2		
92		478.4								747.6		
93		483.8								750		
94		490										
95		496.6										
96		504										
97		512.8										
98		524.8										
99		543.6										
99.5		561										

Sample ID	5-S	5-HS	6-S	6-HS	80/20 bitumen/SCO feed	7-S	7-HS	8-HS	9-HS
Mass%	BP	BP	BP	BP	BP	BP	BP	BP	BP
0.5	72.2	52.2	66.6	36	89	63.6	36	36	52.8
1	131.4	84.4	114.8	68.6	141	112.2	62.8	56.2	81
2	187.2	118.4	173.4	109	193.8	165	108.2	97.8	110.2
3	212	142	201	132.6	215.2	196.6	132.2	123.4	129.8
4	227	163.6	218.2	152.6	229.2	214.8	152.4	142	145.6
5	240	180.6	231	169.4	241.8	227.4	169.2	161.6	161.6
6	251.4	196	243	184.6	252.6	239.2	184.4	176.2	174
7	261	207.8	253.2	198	261.8	249.6	197.8	190	186.6
8	269.6	218	262	209	270.2	258.4	208.4	201.4	197.8
9	278	226.4	270.2	218.6	278.2	266.6	218	211.6	207.6
10	285.8	234.8	278.2	227	285.8	274.2	226	220	216.6
11	292.8	243.4	285.6	235	292.6	281.6	234.2	228	223.8
12	299.2	250.8	292.4	243.2	298.8	288.6	242	235.8	231.4
13	305.2	257.8	298.6	250.4	304.4	294.6	249.2	243.4	238.8
14	311	264.2	304.4	257.4	310	300.6	255.8	250.2	245.6
15	316.4	270.6	310	263.6	315.4	306.2	262.2	256.8	252.4
16	322.2	277	315.4	270	320.8	311.4	268.4	263	258.6
17	327.8	283.2	320.8	276	326.2	316.4	274.2	269	264.4
18	333	289	326.2	282.2	331.2	321.8	280.2	274.8	270.2
19	338.6	294.4	331.4	288	336.4	327	286.2	280.8	275.8
20	344	299.8	336.6	293.4	341.8	332	291.6	286.6	281.4
21	349	305	342	298.6	346.8	337	296.6	291.8	287.2
22	354.2	309.8	347	303.6	351.8	342.2	301.4	296.8	292.2
23	359.2	314.6	352	308.4	356.6	347	306.4	301.8	297.2
24	364.4	319.4	356.8	313.4	361.4	351.8	310.8	306.6	302
25	369.4	324.4	361.8	317.8	366.4	356.4	315.4	311	306.6
26	374.4	329.2	366.8	322.8	371.2	361.4	320	315.6	311.2
27	379.6	333.8	371.6	327.6	376.2	366.2	324.6	320.2	315.6
28	384.8	338.8	376.6	332.2	381.2	370.8	329.2	324.8	320
29	390	343.6	381.6	337	386.4	375.6	333.6	329.4	324.6
30	395.4	348.2	386.8	341.8	391.4	380.6	338.4	333.8	329.2
31	400.4	352.8	391.8	346.6	396.4	385.6	343	338.6	333.6
32	405.6	357.4	396.8	351	401.4	390.6	347.4	343.2	338.2
33	410.6	362	401.8	355.6	406.6	395.6	351.8	347.6	342.8
34	415.6	366.6	406.8	360	411.4	400.4	356.2	352	347.2
35	420.6	371.2	411.8	364.6	416.2	405.4	360.6	356.4	351.4
36	425.4	376	416.6	369	421	410.2	365	360.8	355.8
37	430.2	380.8	421.2	373.8	425.8	415	369.4	365.4	360
38	435.2	385.6	426	378.4	430.6	419.8	373.8	369.8	364.4
39	440.2	390.4	430.8	383.2	435.4	424.4	378.4	374.2	368.8
40	445.2	395.4	435.6	388	440.4	429.2	383	378.8	373.2
41	450.6	400.2	440.4	392.8	445.2	434	387.8	383.6	377.8
42	456	405.2	445.4	397.8	450.6	438.8	392.4	388.2	382.4
43	461.6	410	450.6	402.6	455.8	443.8	397.2	393	387
44	467.4	414.8	455.8	407.4	461.4	449	401.8	397.8	391.8
45	473	419.6	461.2	412.2	467.2	454.2	406.6	402.6	396.4

Sample ID	5-S	5-HS	6-S	6-HS	80/20 bitumen/SCO feed	7-S	7-HS	8-HS	9-HS
Mass%	BP	BP	BP	BP	BP	BP	BP	BP	BP
46	478.6	424.4	466.8	416.8	472.8	459.8	411.2	407.4	401.2
47	484.4	429.4	472.4	421.6	478.4	465.4	415.8	412	406
48	490.2	434.4	478	426.4	484	471	420.6	416.8	410.6
49	495.8	439.4	483.6	431.4	489.8	476.8	425.2	421.6	415.4
50	501.4	444.6	489.2	436.4	495.4	482.4	430	426.2	420
51	506.8	450	494.8	441.4	501	488.4	434.8	431.2	424.8
52	512.2	455.6	500.2	446.6	506.4	494.2	439.8	436.2	429.6
53	517.6	461.4	505.8	452.2	511.6	500	444.8	441.4	434.6
54	522.8	467.2	511.2	457.6	517	505.6	450.2	446.6	439.6
55	528.2	473	516.4	463.4	522.2	511.2	455.6	452.2	444.8
56	533.8	479	521.8	469.2	527.8	517	461.4	457.8	450.2
57	539.8	485	527	475	533.6	522.6	467.2	463.8	455.8
58	545.8	491.2	532.6	481	539.4	528.2	472.8	469.6	461.6
59	552	497.4	538.4	487	545.6	534.2	478.8	475.6	467.6
60	558.4	503.6	544.4	493.2	552	540.6	484.8	481.8	473.6
61	565	509.8	550.4	499.6	558.6	547	491	488	479.6
62	571.4	516.2	556.6	505.8	565.2	553.8	497.2	494.6	485.8
63	578	522.6	562.8	512	571.8	560.6	503.4	501	492.2
64	584.6	529.2	569.2	518.6	578.6	567.4	509.8	507.4	498.6
65	591.2	536.2	575.6	525	585.4	574.4	516.2	514.2	505.2
66	598	543.6	582	531.8	592.2	581.2	522.8	521	511.8
67	604.8	551	588.4	538.8	599	588.2	529.6	528	518.6
68	611.6	558.8	594.8	546	605.8	595.4	536.6	535.4	525.4
69	618.4	566.6	601.4	553.4	612.8	602.6	544	543	532.4
70	625.2	574.6	608	560.8	619.6	609.6	551.4	550.8	539.6
71	632	582.6	614.6	568.4	626.6	617	559.2	558.8	547.2
72	639	590.8	621.2	576	633.6	624.2	567	567	555
73	646	599.2	627.8	583.8	640.6	631.4	575	575.2	563
74	653	607.8	634.6	591.6	647.6	638.8	583	583.6	571.2
75	660.2	616.8	641.4	599.8	654.8	646.4	591.2	592.2	579.6
76	667.6	625.8	648.4	608	662	654	599.6	601	588.6
77	675	635.4	655.4	616.6	669.4	661.8	608.2	610.2	597.8
78	682.4	645.2	662.4	625.2	676.8	669.8	617	619.4	607.2
79	690	655.4	669.8	634.2	684.4	677.8	625.8	629	617
80	697.8	666.2	677	643.4	692	686	635.2	639	627
81	705.8	677.8	684.6	653.2	699.6	694.4	644.6	649.4	637.6
82	714	690.2	692.2	663.4	707.6	703	654.6	660.4	648.6
83	722.8	703.6	700	674.4	715.8	711.8	665.2	672	660.4
84	732.4	718.6	708	686	724.4	721	676.2	684.4	673.2
85	743.2	736.2	716.4	698.4	734	730.8	688	697.8	687
86	750	750	725.2	712.4	744.8	742	700.4	712.4	702.6
87			734.8	728.8	750	750	714	729	720.2
88			746.2	750			729.2	750	741.6
89			750				748		750
90							750		
91									
92									

Sample ID	5-S	5-HS	6-S	6-HS	80/20 bitumen/SCO feed	7-S	7-HS	8-HS	9-HS
Mass%	BP	BP	BP	BP	BP	BP	BP	BP	BP
93									
94									
95									
96									
97									
98									
99									
99.5									