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Article

Proton Nuclear Magnetic Resonance (¹H-NMR) Methodology for Monolefin Analysis: Application to Aquaprocessing-Upgraded Bitumen

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ABSTRACT: Olefins are problematic components of petroleum products responsible for gum formation, polymers, and solid deposition in oil facilities. This work presents a methodology developed for monolefin analysis of whole oils, diluted bitumen, and partially upgraded heavy oils. A proton nuclear magnetic resonance (¹H-NMR) technique calibrated with naphtha fractions of known monolefin contents is proposed. Internal standard addition (IS, dioxane) makes the method independent of the sample C/H atomic ratios (i.e., paraffin/aromatic hydrocarbon ratios). The developed method was applied for monolefin determination of partially upgraded whole bitumen processed under mild catalytic steam cracking (CSC) conditions and is also identified as aquaprocessing (AQP). Large viscosity reductions for AQP-upgraded products (up to 99%) were determined with associated monolefin contents <1.2 wt %.

1. INTRODUCTION

Canadian bitumens and heavy oils like those produced in Latin American countries are viscous materials that routinely require the addition of diluents for lowering their viscosity to make them pipelineable. Current specifications for pipeline transportation in cold countries like Canada are 350 centistokes (cSt) at existing temperature and 19 API gravity.[1] Light diluents could have olefinic components if derived from refining processes. Partially upgraded bitumens can have olefins, whose contents depend on their exposure time to high temperatures and also the type of process, i.e., thermal processing will create larger amounts of olefins, compared to hydroprocessing. Olefins are generally deemed as deleterious components of petroleum products because these are reactive molecules capable of producing polymers, gums, and solid deposits in storage tanks, valves, tubing, furnaces, heat exchangers, and hot refining units. Olefin-derived polymer formation in naphtha and kerosene light fractions has been reviewed,[2] which is also studied by others showing that conjugated diolefins in particular are the most reactive and deleterious components;[3,4] however, also α-olefins have been described to participate in addition reactions with large alkylaromatic compounds, giving origin to insoluble fractions.[5] Mild hydrotreating has been recently implemented as a way to decrease the olefin content of thermally converted bitumen and its derived naphtha fraction.[6,7]

Olefin analysis for light petroleum distillates has been carried out for a long time using high-resolution gas chromatography (HRGC) as described by Gallegos and co-workers for the analysis of pyrolysis gasoline.[8] Routine application of HRGC has been described for the group-type hydrocarbon analysis in terms of paraffins–isoparaffins–olefins–naphthenes–aromatics (PIONA),[9] and HRGC standard methodology has been issued for this purpose.[10] High-performance liquid chromatography (HPLC) has been extensively used for analysis of olefins based on their complexation with Ag⁺ ions immobilized over specially designed olefin columns.[11−13] High boiling components have been analyzed following the described silver complexation;[14] argentation chromatography has been reviewed.[15] Use of supercritical fluid chromatography (SFC) and silver complexation has also been described for olefin analysis[16] and approved as an industrial standard method for this goal.[17] Argentation SFC with mass spectrometry detection (MS) has been used for differentiation of isomeric monolefins and monocycloparaffins.[18] Olefin determination for cracked petroleum products has been the subject of a published review.[19] Conjugated diolefins, those described by others as the most deleterious components,[3,4] were often determined in light petroleum products by the Diels–Alder type reaction with maleic anhydride as described by the time consuming UOP-326 standard,[20] modified by others in order to improve the final titration of unreacted maleic anhydride.[21] SFC with ultraviolet detection (UV) at a specific conjugated diolefin wavelength (240 nm) has been discussed,[22] and the six most common methodologies for conjugated diene analysis have been reviewed.[4]

When analysis of olefins and/or diolefins pertains to the whole oil, bitumen, or their upgraded products, most of the previously described methods do not apply for two important reasons: (1) sample isomerism is so complex that no resolution is achievable and (2) most GC methods fail because of low

analyte volatility, and SFC has solubility issues with the CO_2 eluent. HPLC is a technique that can cope with both issues and thus has been discussed in many instances and subjected to review;[23,24] however, detection and calibration for commonly used nonuniversal HPLC detectors has been the factor hampering its use. The fact that ^{1}H-NMR spectroscopy displays olefinic signals within a spectral range where most petroleum components do not contribute, i.e., from about 4 to 6.3 ppm, has led authors to propose ^{1}H-NMR for the analysis of these unsaturated molecules in both volatile and nonvolatile materials.[4,7,19,25−28] One standard method based on ^{1}H-NMR has been proposed;[29] however, its reliance on a matrix with undefined C/H atomic ratios and the use of a single α-olefin for analysis (1-decene) provide important analysis uncertainty. Use of polydispersed olefin standard mixtures for ^{1}H-NMR calibration purposes has been published;[28] however, the methodology is affected by three issues: (1) there is no sound basis for the selection of standard olefins in calibration mixtures, (2) the C/H atomic ratio of samples (their paraffinic/aromatic ratio, which systematically varies during upgrading sequences, specially hydroprocessing) is not controlled, and (3) integration of whole spectra (large paraffin/aromatic signals plus small olefinic signals) is a source of large error for olefin determination.

This work addresses the development of a ^{1}H-NMR methodology for monolefin analysis of whole oils, diluted bitumen, and partially upgraded heavy oils. Since most olefinic compounds are volatile-low molecular weight compounds as reported before,[27,28] real naphtha cuts and formulated commercial gasolines were selected as olefin sources for calibration purposes. Olefin contents for these light cuts were determined via the standard SFC method.[17] Independence from the sample C/H atomic ratio and better spectral signal/noise (S/N) ratios were achieved via internal standardization with a constant amount of dioxane plus constant sample mass in the solutions submitted to ^{1}H-NMR analysis.

The developed ^{1}H-NMR methodology was applied to the determination of monolefin contents of partially upgraded bitumen processed under catalytic steam cracking (CSC) conditions. The olefin content is one among many quality specifications for partially upgraded bitumen such as viscosity, the distillation range, density, stability, and microcarbon residues that must be achieved for commercial products. AQP competes favorably against hydroprocessing, since the setup operational conditions are milder, i.e., temperature and pressure within the 350−380 °C and 25−35 barg ranges versus 400−430 °C and 100−140 barg, respectively.[30] AQP comprises a single pass of whole oil through a catalytic packed bed thus requiring minimum units (furnace, reactor, and triphasic separator), making this alternative process very attractive, especially since very large viscosity reductions are typically attainable (>98%).

2. EXPERIMENTAL PART

2.1. Samples. One sample of Alberta bitumen was studied in the present work. Logarithm of viscosity was determined within the temperature range comprising 90−200 °C and extrapolated down to 12 °C. The estimated viscosity at this lower temperature was ~1,620,000 cP. AQP was carried out with this feedstock, as described in Section 2.2.

Two refinery/petrochemical naphtha cuts and four formulated commercial gasoline samples were analyzed in the present work. One sample was a pyrolysis gasoline (pygas), and another sample was a cracked naphtha produced within a fluid catalytic cracker unit (FCC).

The pygas sample was stored at 4 °C in the absence of UV−visible light for minimizing solid formation of this extremely unstable sample. The remainder four samples were formulated commercial gasoline samples taken from Calgary gas stations, identified as CGA, CGB, and CGC with end numbers signifying their antiknocking index (octane ratings). A, B, and C imply the oil company producing the gasolines. Interfering additives from formulated gasolines were removed by passing the gasoline samples through an activated silica gel column (see Section 2.6). Silica gel-treated samples were further identified by adding the term SIL at the end of the sample ID.

2.2. Bitumen Aquaprocessing. One bench top unit whose schematic has been presented before[30,31] was used for upgrading the studied bitumen. For the present experiments, the reactor was packed with the NiCeMo-supported catalyst described before;[32,33] an experimental formulation was selected for the tests.[34] Set up conditions spanned from 355 to 375 °C and a pressure of 27 barg, with a fixed weight hourly space velocity (WHSV) of 0.25 h^{-1}. Water (5 wt % based on bitumen feed) was co-injected as steam together with the bitumen and mixed at the entrance of the reactor.

Acidity of the bitumen as determined via the total acid number (TAN)[35] was 1.4 mg KOH/g sample; AQP products spanned the range from TAN values of 0−0.3 mg KOH/g (reductions in the 100−80% range, respectively). AQP products conversions at 550 °C were determined via high temperature simulated distillation (HTSD),[36] spanning the 16 ± 2 wt % range. AQP experiment mass balances were close to ~98 wt %, with liquid fractions 94 wt % and gases 4 wt % on average.

2.3. ^{1}H-NMR. Experiments were carried out at 298 K using a Bruker model Avance III 600-MHz spectrometer, provided with a 5 mm BBFO-Z smart probe. Wilmad 5 mm thin wall precision borosilicate tubes were employed for sample solution analysis. Samples (1.0000 ± 0.0005 g) were dissolved in the CS_2 solvent, brought to 10.0 mL after adding 0.7 mL of C_6D_6 (Sigma-Aldrich 175,870, 99.96 atom %D) plus 1−2 drops of CS_2 solution of tetramethylsilane (TMS, about 20% vol/vol in CS_2). Spectra were referenced using TMS at 0 ppm, with consistent review of the C_6D_6 peak allocated at the corresponding ppm, matching the literature value. Spectra were recorded using a 30° flip angle, applying pulses at 5 s intervals with 200 scans co-added for each spectrum. Pulse sequence applied: zg30. Spectrometer set up parameters: receiver gain (23); relaxation delay (5 s); pulse width (4.1 μsec); spectral width (8417.5 Hz); spectrometer frequency (600.18 MHz). ^{2}H lock (deuterobenzene) and shimming were manually set up. Dioxane (Sigma-Aldrich 266,309, 99.8% purity) was used as an internal standard for quantitative analysis. Dioxane solutions (5.0 μL) in CS_2 (1.0000 g/5.0 mL) were spiked into each sample solution. Exact masses determined with four decimal positions for both the sample and dioxane guarantee analysis independency from sample C/H atomic ratios; improved integration of olefinic and IS signals was achieved under the selected concentrations. Spectra were analyzed using MestreNova Research software; a polynomial fit and manual multipoint base line correction were consistently applied to each spectrum.

2.4. SFC. A Selerity Technologies Inc. (Utah-USA) model 4000 chromatograph provided with flame ionization detection (FID) was used for carrying out group-type SAO analyses (Saturates, Aromatics, Olefins), according to the standard ASTM method.[17] A Selerity Petrosil column 1 mm ID × 50 cm, 5 μm silica particles, and a Selerity 5 cm × 1 mm ID silver-loaded column were used for the analysis. High-purity supercritical CO_2 was used as the carrier fluid and maintained at 200 barg. Elution was achieved at 40 °C. Neat liquid samples were injected with a 60 nL Valco valve. Data handling and processing were performed with EZ Chrom Elite software.

2.5. Gas Chromatography−Mass Spectrometry (GCMS). GCMS was carried out with an Agilent model 6890 chromatograph, provided with a Model 5973 mass spectrometer and also flame ionization detection (FID) in parallel. Signal integration was carried out with the FID, considering a unitary response factor. One PONA methylsilicone Agilent column 50 m long with a 0.2 mm internal diameter and 0.5 μm film was used for analysis, provided with a

Table 1. Properties Determined for the Studied Naphthas[c]

sample ID	group-type distribution by SFC[a] (wt %)			distillation properties (HTSD, T in °C)					density @15.6 °C (g/mL)
	saturates	aromatics	olefins	IBP	5% off	50% off	95% off	FBP	
Crack.Naph	66.3	11.0	22.8	32.6	67.0	135.9	246.1	295.5	0.7508
Pygas	19.4	66.9	13.0	34.6	36.9	110.2	195.5	293.8	0.8222
CGA87	66.4	23.4	10.2	32.6	33.1	95.3	188.9	242.2	0.7165
CGA89	68.9	20.9	10.2	32.6	33.1	93.9	187.7	231.9	0.7146
CGB87	61.1	29.1	9.8	32.6	33.0	102.8	183.8	235.8	0.7168
CGC91	44.2	55.8	BLOQ[b]	32.7	33.5	112.0	183.6	264.8	0.7595
CGA87SIL	75.2	12.6	12.2	34.6	35.6	90.9	185.0	210.0	0.7013
CGA89SIL	76.8	12.0	10.9	33.8	34.1	89.8	189.5	253.6	0.6990
CGB87SIL	69.0	19.6	11.5	33.9	34.1	97.7	191.1	266.0	0.7168

[a]Average of triplicate determinations via supercritical fluid chromatography (ASTM D6550).[17] [b]Below limit of quantification. [c]IBP/FBP: initial/final boiling point. For samples ID: CG means "Calgary gasoline". A, B, and C: Oil company producing the gasoline. Appended number (87, 89, and 91) AKI. SIL means percolated sample through silica gel.

Helium flowrate of 1.2 mL/min under a thermal gradient elution starting at 30 °C (held for 10 min), then ramped to 50 °C at 1 °C/min, held at 50 °C for 50 min, and then ramped to 250 °C at 1 °C/min (held for 5 min at this temperature). Guidelines for GCMS analysis followed the standard methodology.[10] Signal qualitative identification was based on comparison with the National Institute of Standards and Technology (NIST) mass spectral library.

2.6. Polar Hydrocarbon Removal from Commercial Gasoline Samples. Some formulated commercial gasolines were found to contain alcohols and/or other unknown polar additives. These compounds were selectively retained over activated silica gel packed columns (SiO_2 Sigma-Aldrich, P/N 24,217−9, 35−70 mesh particle size, 40 Å pores). Silica gel activation was performed by heating overnight inside an oven kept at 100 °C. Silica gel (25 g) was packed inside a 1.5 cm ID column, achieving a packed density of 0.58 g/mL. Gasoline quantities of 25 mL (about 17.8 g) were run through the column under slight N_2 pressure. The average amount of volatile losses plus retained polar additives and large aromatic compounds was 30 wt %.

2.7. Viscosity Determination. Viscosities were determined with a plate-cone Brookfield viscometer model RV-DP II, provided with spindle numbers 40 (1.6 to 32,000 cP range) and 51 (25 to 512,000 cP range) and a glycol temperature bath (VWR model 1160S).

2.8. Density Determination. Density for liquid samples was determined at 15.6 °C using a Rudolph Research Analytical densitometer model DDM 2911.

3. RESULTS AND DISCUSSION

3.1. Olefin Content Determination for Naphtha Cuts. Olefinic compounds generated during petroleum thermal or catalytic processing are routinely small compounds ($<C_{18}$), mostly originating as fragments from alkyl bridges or alkyl appendages attached to aromatic moieties; consequently, these compounds partition into light distillates (naphtha and kerosene fractions).[27,28] The present work selected naphtha cuts and formulated gasolines with a known olefin content as calibration materials for ^{1}H-NMR monolefin analysis. This calibration is expected to provide more representative olefin mixtures, compared to standardization based on one single compound[29] or based on random olefin mixtures.[28] Real refinery processed cracked cuts produced by processes such as fluidized catalytic cracking (FCC) and pyrolysis, distillation cuts (exposed to mild thermal cracking from tower wall effects), and mild hydroprocessed naphtha components used for commercial gasoline blending are source materials for olefins generated under real operation, deemed representative sources for these components. More realistic sources could be light distillation cuts isolated from different materials produced

from studied upgrading alternatives; however, this alternative was not studied in the present work.

Table 1 presents properties determined for the set of naphtha fractions selected, whose olefin values were determined following standard SFC.[17] Among silica gel untreated samples, the pygas and cracked naphtha have higher densities and contain higher boiling materials, compared to the formulated gasolines that have lower densities and olefin contents, and whose components mostly boil below 200 °C. Pygas showed very high aromatic contents, while the FCC cracked naphtha was enriched in olefins the most, according to the analysis method followed (SFC).[17] Silica gel-treated gasolines were determined to lose aromatic fractions (believed to be the larger molecular weight components), together with the target polar additives, as will be discussed in the next section.

SFC chromatograms for the selected samples are presented in Figure 1. The critical back-flush point (B.F.) for separating saturates from aromatics was found to occur at 5.5 min elution time under the set up experimental conditions; the other cut point between aromatics and olefins is not critical and was set up to occur at 12.5 min. One important observation pertains to the sample presented on panel C, which displayed two artifacts believed to derive from pressure variation during backflushing; these peaks occurred randomly and were not considered for the analysis.

Figure 2 presents SFC retention times determined for standard compounds eluted under the set up experimental conditions. Two sets of results are included: (a) elution time for paraffins only, determined using both columns in series (open symbols) and (b) elution times determined using only the silica gel column, presented for all the studied compounds. Paraffin elution times after passing through both columns in series indicate that all these compounds eluted within the right group-type under the experimental conditions. On the other hand, elution times for several compounds were found to occur outside of the right elution window using only the silica gel column, as observed for three of the analyzed compounds: styrene, dicyclopentadiene, and 1,3-cyclooctadiene. These three molecules eluted inside the aromatic envelope; thus, their olefinic character is not displayed properly by the SFC method.

Figure 3 presents triplicate SFC analyses for the set of studied naphthas and the determined analysis repeatability. The latter is important to consider because the precision derived from SFC determination of olefin contents will directly
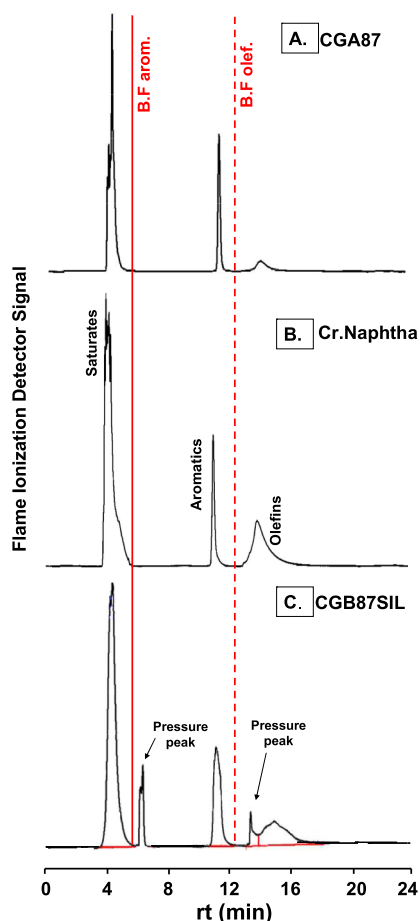
Figure 1. SFC chromatograms for selected studied naphthas.

affect the ^{1}H-NMR results, like those later determined for AQP products. From the preceding, ^{1}H-NMR results following the present approach are affected by 10% relative standard deviation (RSD) only considering the standardization achieved via SFC.[17]

3.2. ^{1}H-NMR Olefin Analysis of Characterized Naphtha Blends and Proposed Calibration for Monolefins in Upgraded Bitumen. Naphthas selected for further ^{1}H-NMR calibration were analyzed for olefin contents via SFC (preceding section). Figure 4 presents the ^{1}H-NMR olefin window (4.5−6.8 ppm) for the selected samples. Five identified monolefin groups were found to be present in all the samples; important contribution from the sixth group pertaining to conjugated diolefins was observed for the cracked naphtha and the pyrolysis gasoline.[7,27] The pygas spectrum was found to be extremely complex, presenting strong signals spanning the whole illustrated range of the spectrum; this finding came as a surprise; however, it was rationalized based on the complex hydrocarbon distribution reported before for another studied pyrolysis naphtha.[8]

Figure 5 presents the details of the olefinic region for the sample CGA87 before and after treating with silica gel. In the present case, oxygenated components (alcohols) are observed to overlap with the spiked dioxane IS signal, thus indicating why for samples like the present one it was found mandatory to remove the additives before running quantitative SFC[17] or ^{1}H-NMR analysis based on internal standardization with dioxane. Treatment with activated silica gel proved successful for the task, as illustrated in Figure 5 for the sample analyzed after

treatment, for which the dioxane IS signal appears unique at 3.5 ppm, whereas before treatment, the alcohol signals were observed to overlap over the IS signal. ^{1}H-NMR has been performed before for gasoline additive analysis.[37]

Known blends were prepared using nonolefin-containing virgin bitumen or lubricant base oil (dearomatized-deparaffinized vacuum gasoil) by spiking known amounts of naphthas characterized in the previous section (known olefin contents), thus covering a wide range of olefin contents (1 to 23 wt %), as shown in Figure 6. Calibrations determined when naphthas were split into two groups are presented in Figure 6: (a) all samples except pygas and (b). only pygas as the source of olefins. Clearly, blends prepared with pygas were found outside the calibration achieved with all the other naphthas. Two reasons were identified for this finding; the first one is that pygas abundant aromatic components were found to severely overlap with conjugated diolefin signals in the ^{1}H-NMR range spanning from 6.6−6.9 ppm. Aromatic and conjugated diolefin overlapping was confirmed by the results presented in Figure 7, suggesting that ^{1}H-NMR does not seem to be suitable for conjugated diolefin analysis. Previously published results agree with this assertion, since conjugated diolefin signals were observed to appear even at lower frequencies over the aromatic hump, which started at 6.3−6.4 ppm for some samples.[28] The second reason derives from the fact that the pygas sample contains many components found to elute outside the correct elution group in SFC, as observed before with the three examples presented in Figure 2.

The pygas sample was analyzed in detail by GCMS following standard ASTM D6733 conditions.[10] Main identified hydrocarbons and their abundances are presented in Table S1. Grouping the hydrocarbon types in terms of saturates, aromatics, and olefins allows a comparison with the results determined before via SFC (Table 1). Table 2 presents this comparison of results. GCMS shows evidence that ∼7 wt % more olefins showed up compared to SFC, comprising conjugated diolefins and cyclic alkane structures having multiple olefin bonds and multiple cycles. In addition, up to 11.2 wt % of mixed olefin−aromatic-containing molecules were identified, which partitioned into the aromatic pool when determined via SFC, thus not revealing their olefinic character via SFC. Two examples presented before in Figure 2 were deemed dramatic, i.e., their high abundance in pygas as determined via GCMS was found to be 4.18 wt % (styrene) and 4.71 wt % (dicyclopentadiene). GCMS analysis for the studied naphtha cuts and gasolines was carried out under standard conditions,[10] showing good agreement with SFC,[17] as illustrated with the results appended for one sample in Table S2 in the supplementary material.

From the preceding results, two conclusions can be drawn: (a) SFC group-type analysis provides unreliable results for molecules containing olefinic moieties together with aromatics and/or multiple monolefinic moieties in cycloparaffinic backbones, despite being components from light cuts and (b) pygas samples cannot be used for ^{1}H-NMR calibration purposes as initially considered in the present work.

Since the monolefin levels existing in AQP upgraded products were found to be low, calibration for the low content end (<4 wt % olefins) was considered in greater detail. Figure 8 presents the results obtained, comprising two scenarios: (a) only monolefins were considered (signals integrated from 4.0−6.0 ppm) and (b) conjugated diolefins included (signals spanning 4.0−6.6 ppm). Figure 8 panel B suggests that
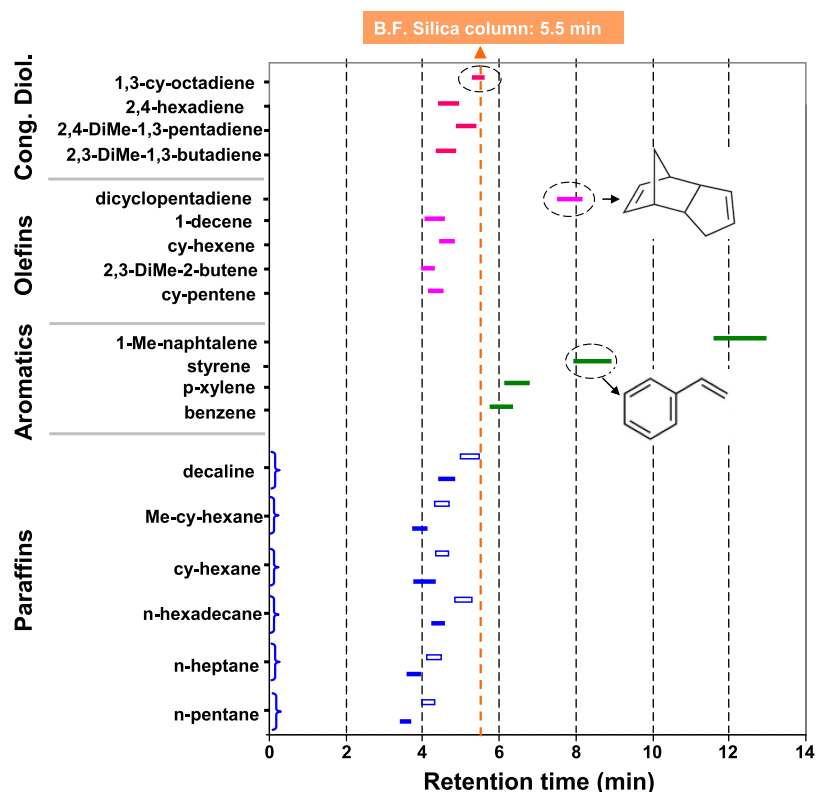
Figure 2. SFC elution time ranges determined for standard compounds. Solid symbols show elution time ranges determined only with the silica gel column. Empty symbols apply only to paraffins, which were in this case eluted from both columns in series (no backflush). Three olefin bearing compounds were found to elute outside their group-type (circled).
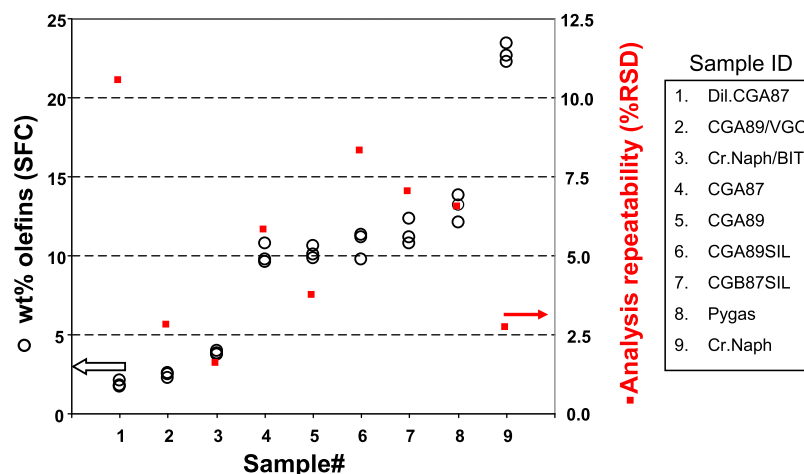

Figure 3. SFC triplicate analysis and repeatability for the studied naphthas.

inclusion of conjugated diolefins produced a calibration not crossing zero over the ^{1}H-NMR signal intensity axis (y), and results interpreted as caused by aromatic signals still appear as a low intensity unresolved hump contributing to this region of the spectra. The correlation expression presented in Figure 8 panel A (eq 1) was used for determination of monolefin contents in AQP bitumen partially upgraded samples.

$$(\text{Area } (4.0 - 6.0 \text{ ppm})/\text{Area dioxane})$$
$$= 1.531 \, (\text{wt\%monolefins}) + 0.3554 \qquad (1)$$

Validation of eq 1 determined based on ^{1}H-NMR spectroscopy was carried out by using a different analysis methodology

that relies on naphtha fraction distillation followed by SFC olefin determination for checking how well the SFC data for the naphtha fit with the ^{1}H-NMR data of the undistilled samples (weighed for the content of naphtha). Figure S1 presents some details for the small home-made distillation unit used for isolating "naphtha fractions", i.e., cuts boiling below C14 (~250 °C). The first aspect required for comparing results from the two methods was the generation of a calibration expression for olefin contents determined for known blends (gasolines spiked over nonolefin-containing bitumen and/or VGO), after isolating their naphtha fractions and running SFC for these. Figure 9 presents the results determined, indicating that a good linear calibration was
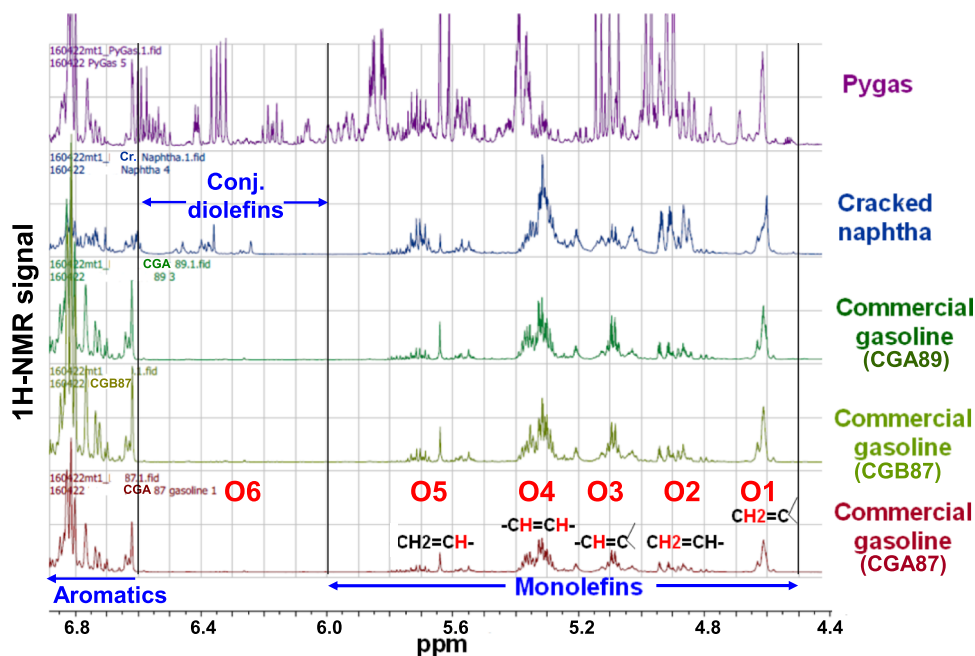
Figure 4. ^{1}H-NMR olefin region from spectra of selected naphthas. Signal assignments taken from published reports: monolefins[7,26,27] and diolefins.[26,28] Olefinic proton groups (O1 to O6) identified as described by Xin et al.[7] and Mondal et al.[27] Spectra referenced using TMS at 0 ppm.
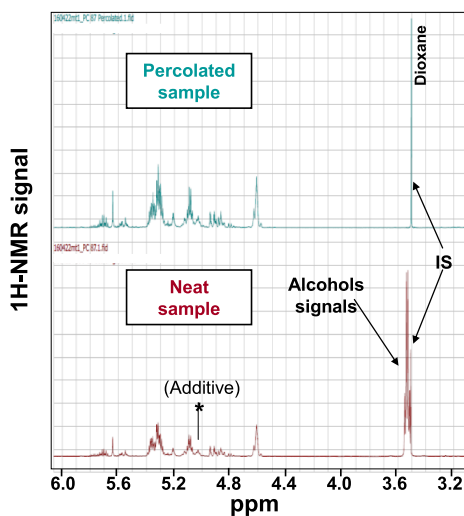

Figure 5. ^{1}H-NMR olefinic region for the sample CGA87 before and after percolation through silica gel. Alcohol signals overlapping with dioxane removed in the present case; other gasoline samples contain another polar additive (unknown nature, appearing at 5.05 ppm), which was also removed with this procedure. Spectra referenced using TMS at 0 ppm.
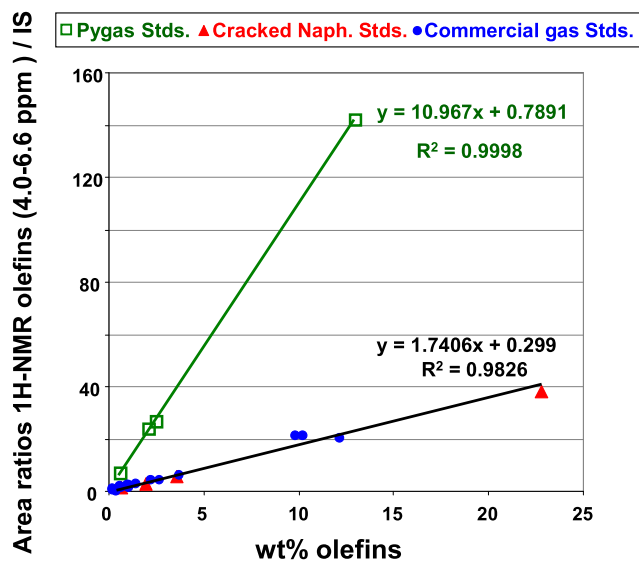
achieved (eq 2). Figure 10 presents olefin content results determined for known sample mixtures that mimic upgraded bitumen. Trends for results determined using both analysis methodologies were found to be similar although underestimated values were found in both cases. Results were determined to deviate more when the combined distillation–SFC method was followed. From the preceding, the present article focuses on the ^{1}H-NMR methodology because with lower requirements (about 3 h required for a single distillation run), the technique provides more consistent results compared to distillation–SFC.

Figure 6. ^{1}H-NMR calibration of olefinic protons (4.0–6.6 ppm) using blends prepared with different types of naphthas having known olefin contents (via SFC).[17]

$$\text{wt\%olefins (distillation} - \text{SFC)}$$
$$= 0.9198 \text{ (known wt\%olefins)} - 0.1127 \qquad (2)$$

From the findings discussed in the present section, three main aspects appear outstanding: (a) pygas composition indicates that this material does not belong to the set of other samples containing olefins and is thus found to be useless for ^{1}H-NMR calibration purposes, (b) ^{1}H-NMR conjugated diolefinic signals appear within a spectral region where aromatics were found to contribute, thus making their analysis not reliable based on this technique, and (c) robust linear ^{1}H-NMR calibration for olefins at low levels (<4 wt %) was determined using real naphtha fractions.
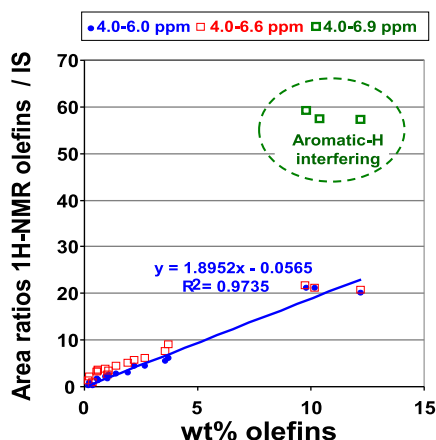
Figure 7. ^{1}H-NMR calibration of olefinic protons using blends prepared with different types of naphthas having known olefin contents (via SFC).[17] The pygas sample was not included in the set of studied naphthas. Olefinic signal integration was carried out setting up different frequency limits: 4.0−6.0; 4.0−6.6; and 4.0−6.9 ppm.

Table 2. wt % Hydrocarbon Group-Types Determined for the Pygas Sample

methodology	saturates	aromatics	olefins
SFC[a]	19.4	66.9	13.0
GCMS[b]	14.7	53.6	(Up to) 31.6[c]

[a]Determined via standard SFC[17] [b]Determined following ASTM D6733[10] [c]Olefins + Diolefins: 20.34 wt %; mixed aromatic−olefinics: 11.26 wt % (See Table S1).

3.3. AQP Upgraded Bitumen and Monolefin Contents.

Partial bitumen upgrading in surface installations has been considered for decades as a feasible pathway for coping with the inconvenient use of diluents for achieving bitumen transportability. Addition of light distillates (diluents) to bring the viscosity and density under specification is routinely practiced worldwide; in Canada, the specifications are 350 cSt at existing temperature and 19°API density determined at "15.0 °C". Cracking followed by mild hydrotreating is commonly described in the open literature for production of diluent fractions.[6,7] However, a simple approach based on CSC, known as AQP (aquaprocessing), has been investigated for long time in our laboratory as recently reported[30] and has also been reviewed by others.[38] A unique and very convenient feature of AQP is that no sample separation (example: distillation) is required, thus making the process a single pass option through a packed catalytic unit where CSC under mild conditions (350−380 °C and 27−34 barg) is carried out. Hydrocarbon partial reforming is achieved during AQP, and hydrogenation reactions help passivating hydrocarbon free radicals and potentially hydrogenating olefins and diolefins, thus minimizing their contributions that lead to lower sample stability and eventual coking.[30]

Figure 11 presents the ^{1}H-NMR spectrum for one sample of AQP upgraded Alberta bitumen, where the frequency markers (tetramethylsilane and deuterobenzene) are visible as well as dioxane internal standard used for quantitative purposes. It is possible to observe that the olefins present in this sample correspond to the groups O1, O2, O3, and O4 following the nomenclature suggested by others before (see Figure 4).[7,27] This finding is deemed important from a process point of view, i.e., the monolefins surviving the process the most were found
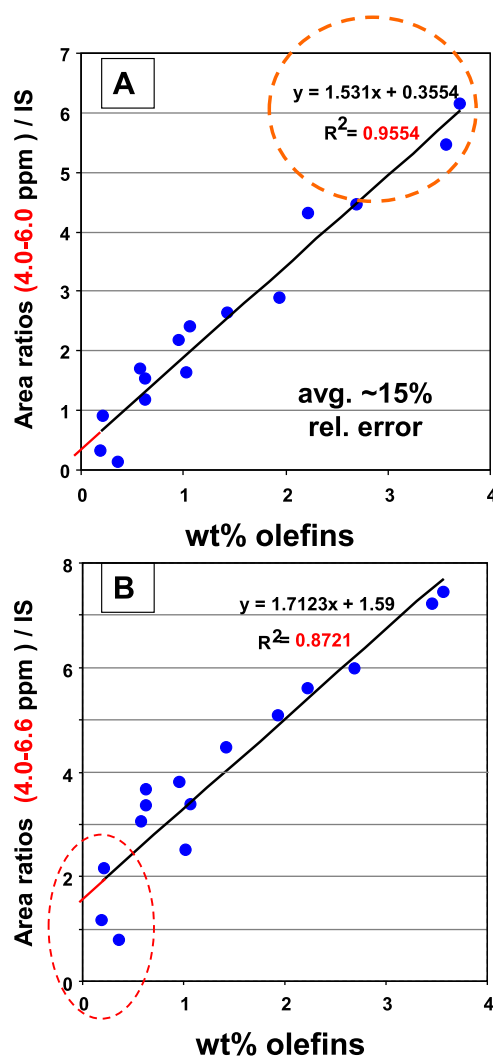

Figure 8. ^{1}H-NMR calibration of olefinic protons for low olefin content samples (<4 wt % olefins) using blends of known naphthas.[17] The pygas sample was not included in the set of studied naphthas. Olefinic signal integration was carried out for (a) monolefins only (4.0−6.0 ppm) and (b) including portion of conjugated diolefins (4.0−6.6 ppm).
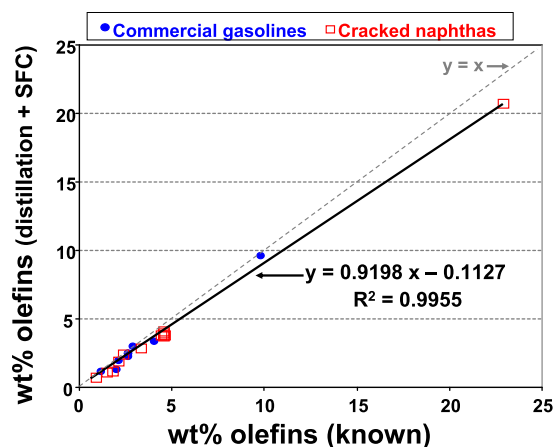

Figure 9. Olefin determination for known samples following a combined distillation−SFC analysis for the naphtha fractions. The same sample mixtures presented in Figure 6 (excluding the pygas sample) were herein studied.
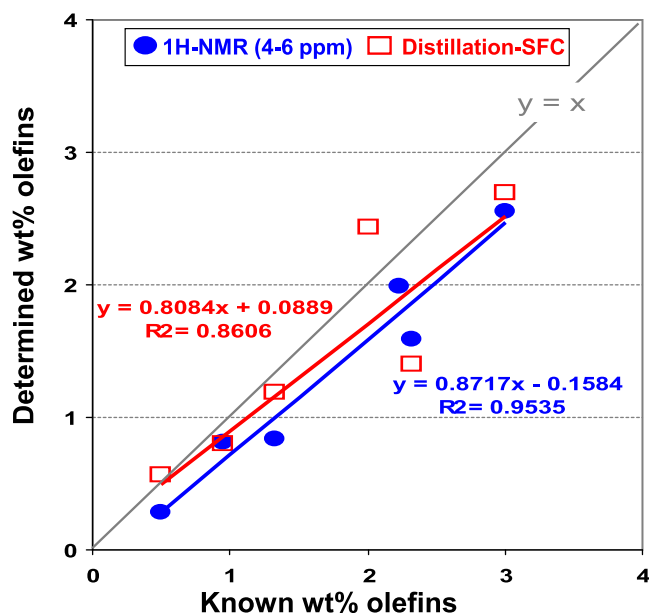
Figure 10. Determined olefin contents for known samples that mimic upgraded bitumen. Analysis performed following the ^{1}H-NMR methodology (eq 1) and combined distillation−SFC for the isolated naphtha fractions (eq 2).

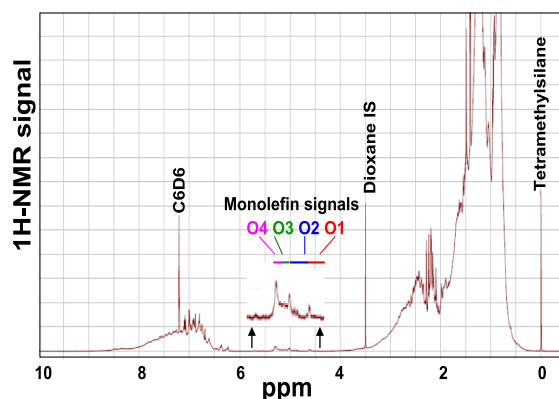**Figure 11.** ^{1}H-NMR spectrum for one product from AQP upgraded Alberta bitumen. Dioxane IS used for quantitative analysis.[28]

to belong to the internal olefin groups O3 and O4, i.e., those described more refractory to convert as reported by others before.[7,27]

Figure 12 presents the monolefin contents calculated for AQP samples using eq 1, plotted as a function of viscosity reduction, which is the most important parameter governing partially upgraded bitumen transportability. Precision of the replicated analyses presented in Figure 12 indicated <11% relative repeatabilities, matching the 10 %RSD reported before for SFC group-type analysis of olefins (see Section 3.1). Important finding provided by the correlation presented in Figure 12 is the noticeable ∼99% viscosity reduction achieved, corresponding to monolefin levels <1.2 wt %. The preceding suggests that about 40% diluent saving one could expect, which is valuable on its own, is achievable with the simple AQP process schematic applied to whole petroleum. Diluent savings could be even better when dealing with heavy oils managed in warmer latitudes such as Central-South American countries for which AQP has been systematically studied in the past decade. However, adjusting all required parameters for achieving
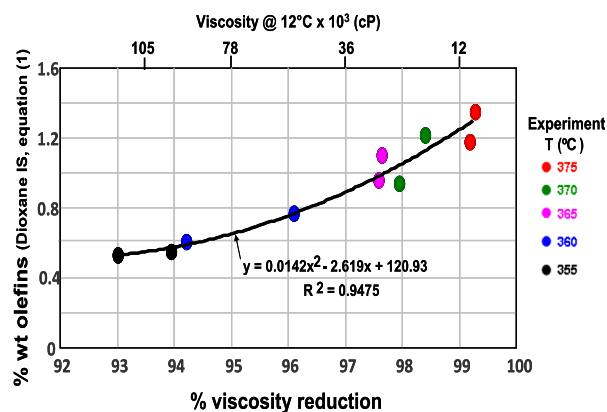

Figure 12. Determined olefin contents for products from AQP upgraded Alberta bitumen. Bench pilot product replicas reported. Analysis performed following the methodology proposed in the present work (eq 1). Results plotted as a function of viscosity and viscosity reduction achieved levels.

pipelining specifications is outside the scope of the present work.

3.4. Polymer and Solid Deposition Affecting Diluted Bitumen and Partially Upgraded Heavy Oil. Preceding sections from this article discussed partial upgrading and dilution for managing heavy oil and bitumen pipelining. General concerns derived from olefin compound presence in diluents and particularly in upgraded heavy petroleum were addressed. The present article described the development of a ^{1}H-NMR methodology conceived and developed for determination of monolefins in whole oil, diluted bitumen, and partially upgraded heavy oil. However, the knowledge thus achieved did not provide any clues about solid deposition potential induced by different levels of monolefins in such samples.

In addition to monolefins, higher solid formation potentials have been reported for conjugated diolefins.[3,4,28] Aromatic conjugated monolefins (styrene, indene, phenalene, and compounds derived with these parent backbones) are also known as polymer precursors, specially phenalenes, which have been studied for decades in relation to gum formation in middle distillates,[39] currently determined based on the ASTM standard method.[40] The presence of styrene and indene derivatives was evidenced in the analyzed pygas sample, the most unstable from the set of studied naphthas in this work. Double resonance ^{1}H-NMR−^{13}C-NMR has been described as a feasible tool for determination of conjugated diolefins,[28] despite the long acquisition times required for ^{13}C-NMR that make the analysis not routine. Double NMR resonance should be also a valid technique for aromatic conjugated monolefins, as suggested by the typical frequencies displayed for olefinic hydrogens in their ^{1}H-NMR spectra: styrene (6.63 ppm),[41] indene (6.55 and 6.88 ppm),[42] and phenalene (6.23 and 6.31 ppm).[43] Alternatively, conjugated diolefins and aromatic conjugated olefins could be analyzed via GCMS following the standard method,[10] applied to the light gasoline−kerosene fractions isolated via distillation, a labor intensive approach by itself.

Further deposition problems could derive from the colloidal instability of samples caused by dilution with paraffin-enriched diluents as well as from partial upgrading processing, which commonly increases the relative proportion of paraffinic components and simultaneously increases the asphaltene

aromaticity. Different techniques can provide clues about these unstable oil composition conditions such as the stability P-value index.[30] Another cause of solid formation is recombination of free radical species, as recently reported for products kept under storage for long periods of time.[44] Understanding of these phenomena could be addressed applying some of the reported "colloidal instability indexes",[45,46] determined based on group-type SARA hydrocarbon analysis (saturates, aromatics, resins, and asphaltenes).[23,24]

From the preceding, sustained-systematic efforts should be dedicated to (1) development of quantitative analysis techniques for the mentioned hydrocarbons involved in solid deposition and (2) development of correlations between their relative abundance and their synergic effects with observed deposition rates and solid deposit amounts. What the present work achieved is a minor contribution within the required set of points that should be addressed for a comprehensive understanding of solid formation.

4. CONCLUSIONS

One ^{1}H-NMR methodology for monolefin content determination in upgraded bitumen was conceived and developed, based on the use of characterized naphtha fractions. Precision of the developed ^{1}H-NMR method was found to be 10% relative standard deviation.

Application of standard SFC group-type analysis was reviewed and used for olefin standardization of naphtha cuts. Among naphtha cuts, those coming from pyrolysis were found to be unsuitable, since these products contain olefinic moieties that partition within the wrong elution window in SFC. SFC group-type analysis for distilled naphtha fractions provided similar results to ^{1}H-NMR, thus suggesting the validity of the spectroscopy method. SFC naphtha analysis was found to be less attractive, demanding higher labor requirements while providing larger result deviations.

Aquaprocessed partially upgraded Alberta bitumen monolefin levels lower than 1.2 wt % were determined, while large viscosity reductions were still achieved (~99%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c00504.

Detailed hydrocarbon analysis for pyrolysis gasoline and commercial gasoline CGC91, determined via standard ASTM D 6733 (Tables S1 and S2)[10] and details of the home-made small distillation unit used for naphtha fraction distillation (Figure S1) (PDF)

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Notes

The authors declare no competing financial interest.

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