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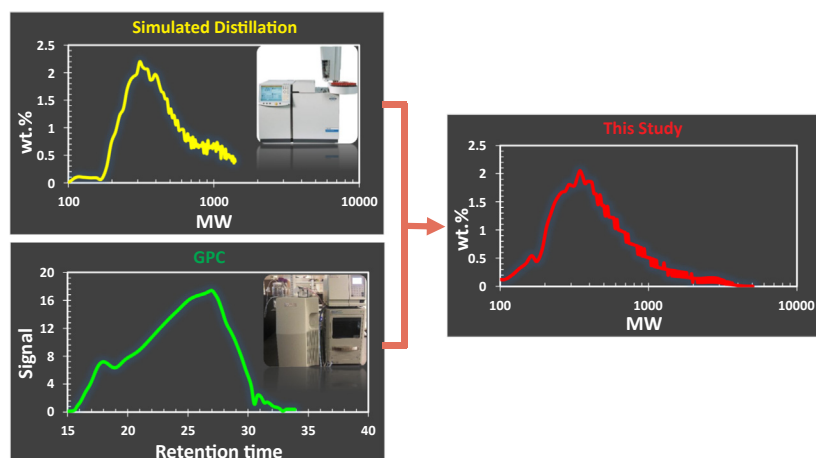
# Characterization of heavy crude oils and residues using combined Gel Permeation Chromatography and simulated distillation

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Characterization of high molecular weight hydrocarbon mixtures such as heavy oil, bitumen, and vacuum residue is essential to design and optimization of the recovery, upgrading, and transportation processes. Characterization provides information about the boiling point and molecular weight distributions. To obtain these information, developing the simple, fast, and consistent characterization method is needed. In this work, for the first time, we combine Gel Permeation Chromatography (GPC) and Simulated Distillation (SD) results to characterize very heavy hydrocarbon samples. In the proposed characterization method, each sample is used individually as a standard sample for GPC calibration by properly matching SD and GPC results. In the other words, use of a standard sample, which is usually polymer compound and not appropriate representative for oil samples, is avoided. The GPC and SD results are coupled to generate the calibration curve that correlates the retention time and molecular weight. Employing the obtained calibration curve for each sample and having the GPC results, the whole molecular weight and boiling point distributions are obtained regardless of the complexity of the extra heavy sample. The proposed characterization method is validated using a known standard sample. Next, this method is applied to obtain molecular weight distribution of several bitumen samples and the bitumen fractions. The developed characterization method provides a tool to find a better understanding of the molecular weight and boiling point distributions of complex mixtures.

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**Nomenclature**

FTIR	Fourier transform infrared
GPC	Gel Permeation Chromatography
HPLC	High performance liquid chromatography
LS	Light scattering
MW	Molecular weight
NMR	Nuclear magnetic resonance

Off (%)	Percentage of eluted components from GC
RI	Refractive index
RID	Refractive index detector
SARA	Saturate aromatic resin asphaltene
SD	Simulated distillation
t	Retention time in GPC columns
THF	Tetrahydrofuran
Wt.%	Weight percent

**1. Introduction**

Molecular weight distribution is a very useful tool for characterization of complex mixtures such as heavy oil and bitumen samples. This information is also important for computational thermodynamics and phase equilibria of the hydrocarbon systems [1,2]. There are several well-established methods for characterization of conventional crudes such as ASTM D2887 and D1160, in which the conventional oils can be well characterized. The recognized method to characterize the heavy crudes is simulated distillation (SD) under standard of ASTM D7196. The boiling point distribution up to a temperature of 720 °C can be obtained using ASTM D7196. However, heavy and extra heavy crudes such as bitumen and vacuum residue do not elute completely from the gas chromatography (GC) column. For example, only about 80% of Athabasca bitumen elutes from GC column [3]. The un-distilled part plays a critical role in study of asphaltene precipitation, coke formation, and thermal cracking processes.

Although measuring boiling point distribution is preferred to molecular weight distribution, it is not feasible in case of complex mixtures such as extra heavy oil and bitumen samples and almost half of the sample remains undetected in the form of residue. Moreover, before boiling, some of hydrocarbon molecules crack at high temperatures. For these components, degradation temperature is lower than their boiling temperature. Thus, they cannot be recognized and characterized using methods prone to high temperature conditions.

Many attempts have been made to characterize crude oils such as atmospheric and vacuum distillation [2], simulated distillation [1], Gel Permeation Chromatography [4–6], HPLC [4], SARA (saturate aromatic resin asphaltene) analysis [7], and supercritical fluid extraction [5,6,8]. Distillation is the preferred method in refining as it is feasible and economical and also provides extensive information about the oil fractions [2]. However, laboratory distillation methods can be carried out at temperatures up to 350 °C to prevent the possible thermal cracking and decomposing problems [8,9]. For conventional oil samples, this type of distillation can be more practical as the atmospheric and vacuum distillation methods such as ASTM D86, D1160, and D2892 characterize 80–95 wt% of the oil [2]. However, for heavy and extra heavy oil, the conventional distillation methods can provide information about a small fraction of the sample. Even the new developed high vacuum distillation methods cannot distill more than 60 wt% of heavy oil and natural bitumen samples [2,10]. Increase of solvation power of a solvent near its critical region was employed to fractionate heavy oil and vacuum residue samples in supercritical fluid extraction method. However, to characterize the obtained fractions, various analyses must be performed including elemental analysis, density and viscosity/temperature relationship, molecular weight by Vapor Pressure Osmometry (VPO) and Gel Permeation Chromatography (GPC), boiling point curve by GC, SARA analysis, and H NMR (proton nuclear magnetic resonance) [5,6,8]. In other fractionation methods such as SARA analysis, the compositional analysis of oil samples also produces inadequate and inconsistent information. Chemical-based analysis of heavy oil and bitumen is not only inconsistent, but also applying further

characterization tests on obtained fractions is time and cost intensive.

Rodgers et al. [11] presented a correlation for predicting the molecular weight distribution of high boiling hydrocarbon mixtures. They used GPC elution volume, hydrogen to carbon ratio obtained by elemental analysis, and hydrogen distribution ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) from NMR spectroscopy. This method seems expensive and complicated. Because it is necessary to have sufficient fractions of oil from GPC and obtain hydrogen to carbon ratios and hydrogen distributions, which requires extensive analytical data including NMR and elemental analysis measurements. Peramanu et al. [12] measured the molecular weight distribution of Athabasca and Cold Lake bitumen samples and their SARA fractions using calibrated GPC with polystyrene standards. They verified the results using VPO measurements and found the correction factor for GPC distributions. Huang and Radosz were also corrected the obtained molecular weights from GPC to compensate the impropriety of polystyrene as standard and make the GPC-derived results consistent with VPO [13].

Champagne et al. [14] compared the Athabasca bitumen molecular weight distributions obtained by different solvent types and measurement techniques. They reported that the GPC method is not suitable for determining the molecular weight distribution of bitumen as a mixture of many different structures because no single calibration curve could be obtained. GPC-HPLC method was also developed by Stringano et al. to characterize monomeric to polymeric polyphenols in which single calibration curve was obtained [15]. GPC was also employed to characterize crude oils by Oelert et al. [16]. GPC together with other methods such as VPO, HPLC and various spectroscopy methods has been also used for characterization of asphaltene and oil heavy component [17–19]. Moreover, the GPC-Fourier transform infrared (FTIR) and GPC-Light scattering (LS) detection have been used to characterize polymer samples [20,21]. Recently, Lavric et al. determined molar masses of macromolecules using GPC-LS having the molar mass of an arbitrary calibration standard in the same solvent [22].

In this work, our goal is to establish a general method in which the whole molecular weight or boiling point distribution of complex mixtures such as bitumen and heavy oils can be obtained by coupling the results of the simple, fast, and low cost analytical tests; SD and GPC. Combining the two characterization methods, the molecular weight or boiling point distribution of bitumen and heavy oil samples and even more heavy compounds like asphaltene and vacuum residue is achieved. GPC benefits from high reproducibility, short run time, which results in low labor costs, and ability to be applied on a wide variety of sample types even thermally sensitive compounds [16].

In the following, the methodology of the present characterization method is described, validated, and employed to characterize a bitumen sample. Then, characterization of Athabasca bitumen and its fractions obtained by vacuum distillation and solvent fractionation methods are discussed followed by conclusion.

**2. Methodology**

GPC is a form of liquid chromatography and one of the versatile

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