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HEAVY OILS - A REVIEW

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ANALYTICAL METHODS FOR DETERMINING MOLECULAR WEIGHT
OF COALS, BITUMENS AND HEAVY OILS
A REVIEW

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ABSTRACT

This report reviews current methods used for determining molecular weight of fossil fuels. It emphasizes the strengths and weaknesses of the different methods when applied to the types of samples that may be encountered in upgrading research.

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METHODES ANALYTIQUES DE DETERMINATION DE POIDS MOLECULAIRE
APPLICABLES AUX CHARBONS, BITUMES ET HUILES LOURDES

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RÉSUMÉ

Ce rapport regroupe les différentes méthodes analytiques utilisées pour la détermination du poids moléculaire moyen des combustibles fossiles. L'emphase est mise sur les forces et faiblesses de chaque méthode lorsque appliquée au type d'échantillon rencontré en recherche sur la valorisation.

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1- Introduction

Molecular weight is an important parameter in the characterization of feed samples encountered in upgrading low grade fossil fuels into transportation fuels. Molecular weight gives an idea of the average molecule present in the feed. Used with other information, it could be used to determine the type of conditions needed for successful upgrading.

However, the usefulness of this information is reduced by the fact that the molecular weight determination methods often disagree on the absolute value associated with a particular sample¹. The present report reviews the different methods used for MW determination of fossil fuels and emphasizes the strengths and weaknesses of each technique.

In this report, analytical techniques have been grouped in four categories depending on the type of properties used as a basis for measurement:

- Colligative properties:
 - osmometry
 - cryoscopy
 - ebullioscopy
 - isothermal distillation
- Transport phenomena:
 - ultracentrifuge
 - viscosity
 - diffusion
- Spectroscopy
 - nuclear magnetic resonance
 - mass spectrometry
- Chromatography
 - liquid chromatography
 - simulated distillation

A fifth category groups mathematical methods based on correlation with physical and chemical properties. It can be noted that several of these methods have been adapted from polymer analysis methods since heavy crudes can have properties similar to polymers.

2- Colligative properties

Colligative properties are dependent on the number of particles present in the sample and it can be demonstrated that the measurement of any colligative property always yields the number average molecular weight (M_n)^{2,3}. Methods covered by this category are vapour phase osmometry, cryoscopy (or freezing point depression), and ebullioscopy (or boiling point elevation).

a) Osmometry

Classical membrane osmometry uses the osmotic pressure difference between two solutions to calculate the molecular weight. Variations in osmotic pressure between a sample and a reference solution across a permeating membrane could be measured by monitoring liquid levels in capillaries. Although this method gives

reliable data for heavy polymers, it is not suitable for low mass polymers (<15000 daltons)². Therefore it cannot be applied to crude oils and will not be discussed further in this report.

Modern vapour phase osmometry (VPO) uses the difference in vapour pressures between a sample solution and pure solvent to calculate the solute average molecular weight. Two thermistors are placed in a vapour saturated cell. When solvent drops hang from the thermistors, the temperature difference is zero. If a solution drop replaces the solvent drop on one thermistor, solvent vapour condenses to dilute the solution. Heat resulting from the condensation process generates a temperature difference between the thermistors. Since this temperature difference is dependent on the molality of a solution, i.e., the number of moles of solute per unit mass of solvent, it is possible to calculate the number average molecular weight of the solute².

This method is especially suitable for low molecular weight solutes since the temperature difference (thus the sensitivity) is inversely proportional to the molecular weight. Because of the simplicity of the method, vapour phase osmometry (VPO) is very popular for the MW determination of fossil fuels, coal liquids and humic substances⁴⁻¹⁰. However, measurements are dependent on solvent, concentration and temperature. Influence of solvent is partly due to solvent-solute interactions like dipole-dipole interactions, hydrogen bonding and charge transfer complexes⁸. Moschopedis et al¹¹ have also related VPO results to the dielectric constant of the solvent. Solute-solute interactions are also possible because of the polar nature of the samples, especially when the solutions are concentrated. If it is the case, molecules tend to agglomerate leading to significant error in estimation of the molecular weight. It is also important to note that the theory of the method is based on ideal solutions (infinite dilution). However, because of sensitivity, there is a limit on the low concentration (typically 1-10% by weight) that can be used which has an influence both on the ideal behaviour of the hardware and on the occurrence of undesirable interactions. About the concentration effect, Chung et al⁵ reported that the relation between concentration and voltage differential ("readings") can be linear or curved depending on the concentration range. If the relationship is different for the standard concentration range compared with the sample concentration range, this can lead to significant errors in MW values. Finally, the MW determination is dependent on the temperature at which the measurement is made^{8,11}.

b) Cryoscopy and ebullioscopy

These two methods are based on the fact that phase transition temperatures of a solution are affected by the concentration of the solute^{2,3}. As the concentration increases, the liquid state range increases, i.e., normal freezing point decreases and normal boiling point increases. As with osmotic pressure, the temperature variation is approximately proportional to the molality of the solution and inversely proportional to the number average molecular weight.

In ebullioscopy (or ebulliometry), a solute is dissolved in a liquid, resulting in a vapour pressure reduction directly related to the solvent activity. An increase in temperature is then required to bring the vapour pressure of the solution back to atmospheric pressure, and this boiling point elevation is directly related to concentration and molecular weight. In polymer analysis, the principal problem of ebulliometry arises from superheating which

raises the observed boiling point above its true thermodynamic value. Methods have been described to overcome this problem². Since the boiling point of a liquid is dependent upon pressure, ebullioscopy is also sensitive to pressure change. This led to the development of differential measurement instruments to improve on the accuracy of the method. Application to crudes and bitumens¹² raises additional concerns as for VPO, i.e., concentration limits and solvent-solute or solute-solute interactions. In addition, the presence of low boiling fractions interferes in the measurement of molecular weight because of evaporation losses. Therefore, ebullioscopy is not very popular for analysis of fossil fuels.

Cryoscopy is closely related to ebullioscopy. Calculations are similar except that the freezing point depression is monitored. Since the cryoscopic constant is usually greater than the ebullioscopic constant, this method generally offers greater sensitivity. One major problem is to ensure that the solute will not precipitate at temperatures close to the freezing point. Similarly to ebullioscopy, supercooling of the solution can be problematic and high concentrations and molecular interactions can cause significant errors. Cryoscopy has been used to some extent in characterization of fossil fuels¹³⁻¹⁷. As for VPO, MW values are also dependent on concentration and solvent type and high values for asphaltenes may be due to molecular aggregation¹³.

Of the three methods mentioned here, only VPO and cryoscopy would be suitable to samples containing low molecular weight components and thus would be suitable to whole crudes. Since these methods depend on solubility, one must be careful that the sample is well dissolved before making any measurement. Because of the simplicity of the method and instrumentation and of its applicability to a wide range of materials, VPO is the most popular colligative property method used in fossil fuel characterization.

c) Isothermal distillation

The main difference between VPO and isothermal distillation is that larger amounts of solution are maintained under isothermal conditions¹⁸. It is postulated that the speed of distillation is proportional to the difference in vapour pressures of the two solutions that are compared. The speed of distillation is measured by the movement of unbalanced scale arms vs time. It has been found that the relation between the speed of distillation and the concentration is linear if the differences between the molar concentrations are small. Like most of the methods covered in this report, this method has been developed for polymers. However, it has also been checked for low MW compounds and low MW polymers and accuracy was within experimental error ($\pm 5\%$). Results were comparable to cryoscopy. Disadvantages of this method are time-consuming measurements and limited choice of solvents²⁰.

3- Transport phenomena

Some MW determination methods depend on properties of solution related to flowing or transport properties. These methods include ultracentrifugation (sedimentation), diffusion and viscosity. While sedimentation and diffusion are related to the motion of molecules through a stationary solvent, viscosity is a measure of the relative motion of the different components of the whole solution.

a) Ultracentrifuge

Ultracentrifugation is based on the sedimentation of molecules originally dissolved in an homogeneous solution. A special optical system in the centrifuge measures the local concentration as a function of radius. There are two methods of measuring the molecular weight from sedimentation²: the sedimentation velocity method and the sedimentation equilibrium method. The first one uses high speed and measures the rate of sedimentation. The second one uses lower speed at which sedimentation would equilibriate with diffusion. In this case, the instrument measures the concentration gradient established at equilibrium. This method is most often used. The sedimentation rate or sedimentation concentration gradient can be related to the weight average molecular weight (M_w). In theory, other MW averages (M_n , M_z) can be calculated but in practice, calculations are tedious. Other limitations are the time requirements (up to 40 hours) and the need to apply complex corrections in many cases. The other major problem with oils is the presence of low molecular weight species.

b) Viscosity

In polymer analysis, viscosity is often used to measure molecular weight. Even dilute solutions of polymers have a high viscosity which easily distinguishes them from solutions of low MW species. The specific viscosity is a measure of the relative increase of time taken by a known volume of solution to go through a capillary as compared to pure solvent. The intrinsic viscosity can then be calculated as:

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \frac{K \sum N_i M_i^{1+a}}{\sum N_i M_i}$$

The viscosity average M_v is then calculated from:

$$M_v = \left[\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right]^{1/a}$$

Since 'a' lies generally between 0.5 and 0.8, then $M_n < M_v < M_w$ so that M_v is not related to any other MW average. This does not help for comparisons between MW values. Other limitations are^{2,21}:

- M_v is dependent on solvent and temperature because 'a' is an experimental parameter.
- Low MW species are not easily determined because the difference in viscosity is hardly detectable.
- M_v is also dependent on the type of sample which does not help calibration and analysis of oil and bitumen samples.
- 'K' and 'a' constants cannot be determined accurately for oil, residue or asphaltene samples.

c) Diffusion

This method is based on the band broadening effect that occurs when a sample flows through a capillary tubing due to the diffusion of molecules towards solvent surrounding the solute band. It has been shown that the extent of band

broadening can be related to the molecular weight of the solute. The instrumentation is similar to HPLC apparatus except that the column is replaced with a capillary tubing having an internal diameter similar to that of connecting tubing used in HPLC (approximately 0.02")²²⁻²⁴. Measurements are done in a portion of the chromatographic Van Deemter curve²⁵ where the contribution from unwanted terms is negligible so that the diffusion can be directly related to the number of theoretical plates. The diffusion is assumed to obey a Gaussian function. When these two conditions are met, the logarithm of the diffusion (log D) is linearly related to the logarithm of the molecular weight (log M) and yield a density average molecular weight, M_d .

The method has been used for polymer^{22,23} as well as crude oil²⁴ samples and a relation between M_n , M_w and M_d has been determined allowing the calculation of one value from the two others thus allowing comparison between methods²³. But the experimental conditions have to be carefully controlled. In addition to the conditions stated above, the flowrate must be carefully optimized to ensure a proper elution profile approaching that of a Gaussian curve²². The length of the capillary tubing is important because it directly affects the precision of measurement on the peak width. Also, although it would not be a problem with oil or residue samples, very high molecular weight species might have unusual flow properties in capillary tubing due to higher friction and viscosity. Finally, the system would be subject to the same type of concentration problems encountered in other methods where the sample is diluted in a solvent.

4- Spectroscopy

Spectroscopic methods can also provide a way of calculating or estimating the molecular weight of oils and coals. These methods usually involve some computation from information given by the spectrum acquired from the samples.

a) Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (NMR) is a technique providing information on the composition of samples, i.e., on how atoms within a molecule are arranged relative to others. ¹H- and ¹³C-NMR can inform about aromatic-aliphatic content, presence of various functional groups, and types of chemical bond present. On single components, this can lead to the elucidation of the molecular structure. On complex samples, it gives some information on the different atomic environments present in the sample molecules.

In order to calculate the molecular weight, calculations use information on terminal functional groups and their relative concentration compared to non-terminal groups²⁶. Limitations of this method are:

- many assumptions and shortcuts are used to approximate the MW value;
- results are not as reliable as other less complicated and more popular methods;
- technique is costly and necessitates an experienced operator;
- extensive calculations are needed.

b) Mass spectrometry

In mass spectrometry, sample molecules are ionized and the produced ions are discriminated according to their mass/charge ratio. Among the several

ionization techniques, three can provide mass distribution because produced ions are not extensively fragmented into smaller ions: field ionization mass spectrometry, low voltage electron impact MS and chemical ionization MS²⁵.

i) Electron impact (EI) and chemical ionization (CI)

In the EI mode, molecules are ionized when crossing a beam of electrons. Produced ions are transferred to the mass analyzer which gives their m/e ratios. Usual EI (70eV) spectra show extensive fragmentation but a lower voltage (10-20 eV) can be applied to reduce its extent and mainly produce molecular ions. Thus molecular weight can be estimated²⁷. However, response factors are not the same for all components and some aliphatics undergo non negligible fragmentation even at low voltages; thus, calibration might be problematic.

Low voltage/high resolution mass spectrometry on magnetic sector instruments (LV/HRMS) has also been used for MW determination. Although its primary use is to give detailed compositional analyses²⁸⁻³⁰, the generated data can be used to obtain MW information. The major problem with LV/HRMS is the lack of sensitivity which can lead to repeatability problems. Lumpkin and Aczel²⁸ also mentioned that the method gives better results with double bond compounds than with saturated compounds as in low resolution EI instruments. Finally, high resolution instruments are very costly.

In the CI mode, a gas is introduced in the source with the sample. This reactant gas undergoes EI in order to produce reactive ions which react with the sample molecules to produce mass spectra. CI spectra have a fragmentation pattern intermediate between the simple FIMS spectra and the complex EI spectra. Also, the addition of gas molecules, e.g., CH₄, isobutane, is not 100% effective. Because of these shortcomings, the technique is very seldom used for the purpose of molecular weight calculation of complex samples although it can provide a good estimate of the molecular weight distribution^{31,32}.

ii) Field ionization MS (FIMS)

In FIMS, the whole sample is introduced in the system and the source is heated in order to gradually introduce molecules in the mass analyzer. The molecules are ionized by an electric field strong enough to remove one electron. Usually, there is little or no fragmentation of the ion. FIMS provides the simplest mass chromatograms consisting of almost exclusively molecular ions. Thus, it represents the true mass distribution of sample components. Of course, the main advantage of FIMS is that it provides a distribution of material which allows the determination of several MW averages (M_n , M_w , M_z) that can be compared to other methods.

The technique is best suited to high molecular weight materials. It can be used to study heavy oils, bitumens and pitches^{27,33,34}. It has been noted that FIMS yields somewhat lower MW values than more popular methods. Of course, FIMS has the advantage of avoiding concentration problems that are seen with other methods where the sample is diluted in a solvent. But it has also been recently reported that asphaltenes are composed of large molecules that entrap smaller molecules³⁵. These new data might explain some of the discrepancies between MW values. Indeed, these large entities would be analyzed as one species by most methods while FIMS would separate

them into their components.

Field desorption (FDMS) is a variant of FIMS that can also be used for molecular weight distributions with basically the same advantages and disadvantages. Both methods gave consistent results for a variety of crude oils³⁴ although FDMS is sometimes considered less reproducible³³.

5- Chromatography

Chromatographic techniques have the same advantage as FIMS, i.e., yielding a distribution of sample components and requiring only a small sample. However, they are time consuming experiments when compared to techniques such as VPO.

a) Liquid chromatography (LC)

Both reverse phase and normal phase LC can be used to monitor the distribution of components in a sample. However, due to the nature of packings used in these techniques, the distribution is not really related to molecular weight or size but rather to the degree of interaction of the components with that particular packing. Indeed, high performance liquid chromatography (HPLC) has been used to monitor changes in samples before and after treatment or to compare selective fractions from sample to sample³⁶. But in these cases no calculation of molecular weight was attempted.

Size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC), has been developed specifically for molecular weight calculations. Because of the special nature of SEC packings, solute-packing interactions have been kept to a minimum and the elution of the components is mostly related to the hydrodynamic volume, i.e., size and shape, of the molecules²⁵. For polymer analysis, these statements are valid. But in complex samples such as crude oils, residues, and asphaltenes, molecules have different polarities and properties and elution times vary with the type of molecules because the packing is not completely inert¹. Nevertheless, the method has been applied to pitches^{37,38}, coal liquids³⁹⁻⁴⁰, residues⁴¹, asphalts⁴², and asphaltenes⁴³.

In addition to the packing problem, other aspects affect the accuracy of the MW results⁴³. Of course, as for other methods where dilution in a solvent is involved, concentration problems such as aggregation and precipitation and solvent problems such as association could arise. Also, calibration is problematic because no standards of similar composition are available. Calibration is usually based on narrow polystyrene standards that could have elution characteristics different from those of the samples due to different interactions with the packing. Finally, the common detectors are not directly sensitive to sample mass so the response factors of the different components can be very different⁴⁴. Bartle et al⁴⁰ reported that in SEC of coal derivatives, general SEC errors could cause up to 3% deviation while errors associated with the nature of the sample could be in the order of 2-40% from detectors, 50-100% from the calibration, and up to 200% from the solvent.

Despite these inconveniences, SEC is still very attractive because it is one of the few methods that gives a distribution and it is inexpensive compared with mass spectrometry. For this reason, it has been very popular for comparative

studies between feedstock and product compositions, even though absolute values would not be measured. It has been mentioned that secondary interactions could result in improper calibration and differences in elution of the various components of a sample. However, conditions can be found to minimize these interactions⁴⁵. Under such conditions, only a small portion of oxygenous compounds would elute earlier than expected due to solvent-solute association. Therefore, SEC can be used to generate useful numbers except maybe for coal liquids where oxygen is present in higher concentration.

It must also be mentioned that SEC has been coupled to a wide variety of detectors in order to improve the validity of the detection or to combine two MW determination methods. Usual detectors are the refractive index and the UV. These along with the evaporative detector have been assessed earlier⁴⁴. That report showed that no detector is ideal and that the evaporative and refractive index detectors give complementary results. For polymers, novel approaches have been developed such as universal calibration by coupling SEC and viscometry^{46,47} or SEC and densitometry⁴⁸. These methods were never demonstrated with oil samples partly because the variation of viscosity or density for small MW molecules is very small if not negligible. In polymer analysis, light scattering⁴⁹ is very attractive. Low angle laser light scattering (LALLS) can be used by itself to determine M_w values or coupled to SEC for the calculation of M_n and M_w . However, LALLS is limited to $MW > 2000$ and therefore is not applicable to oil samples or distillation residues. High MW asphaltenes can be determined but only if no small molecules are present. The method has also been applied to high MW coal derivatives⁵⁰ as a stand-alone method.

b) Simulated distillation

Simulated distillation has been widely used in the petroleum industry to determine the boiling point distribution of distillates. This technique uses gas chromatography to gradually elute components in distillates as their boiling point increases. Previous work in this laboratory⁵¹ has shown that for the same class of non-polar components (aromatics or aliphatics), molecular weight is directly related to boiling point via the retention time. Based on this, molecular weight distribution was estimated for mono-, di-, and polyaromatics of middle distillate and gas oil fractions for which the molecular weight distribution was linear. The method was not applied to naphthas because of non-linear relationships. Since the method provides a distribution, several types of MW average (M_n , M_w , etc.) can be calculated as for SEC.

The method is limited to distillates and relatively light residues because of the limitation from the GC operating temperature. This could be overcome by using a High Temperature SimDist apparatus or a Supercritical Fluid Chromatography system (SFC) which could both chromatograph high molecular weight compounds. Preliminary work with distillate model compounds in SFC showed that the polar and aromatic fractions all lie on the same calibration curve; only saturated compounds lie on a different curve⁵². This means that MW could be estimated with reasonable accuracy if the concentration of saturated components is low. Runs are shorter than with SEC or FIMS and resolution is better than with SEC.

6- Correlation methods

Several correlation methods have been developed for petroleum and heavy oil fractions⁵³⁻⁵⁶. These correlations have been designed to calculate the average molecular weight of distillate fractions and therefore do not provide any MW distribution. However, they are based on standard tests that are routinely performed on these samples, such as viscosity, boiling point distribution (from SimDist), or specific gravity. Correlations have been checked with model compounds and with known samples. Results show that they can be reasonably accurate with distillates but are less accurate with higher molecular weight fractions. Other problems are that they are empirical equations that could be different for different types of samples. Also, these equations are based on 'known' molecular weights of given samples which might be based on methods that did not provide accurate results.

7- Comments and summary

This report showed that several types of molecular weight values can be determined and that results from only a few methods could be directly compared. MW values from colligative properties methods (VPO, cryoscopy, ebullioscopy) yield number average molecular weight (M_n) and can be compared to SEC and FIMS. Light scattering and ultracentrifugation could also be compared to SEC and FIMS but for M_w . Other methods yield unique average molecular weights (diffusion, viscometry) that are difficult to compare with other methods. In some cases (ultracentrifugation, isothermal distillation), methods cannot be directly applied to oil samples.

Some methods can measure several types of average molecular weights because they provide a distribution that allows calculation of M_n , M_w or M_z . These methods, namely SEC and FIMS, have a definite advantage because of their versatility and of the extra information on the composition of the sample. SEC is attractive because of the low cost and ease of use but conditions (solvent, column packing, concentration) must be selected carefully.

Although it does not provide information on the distribution of materials, VPO is also very attractive because the method is very simple. Its main drawback is that MW values can vary if the solvent is changed. The solvent and concentration must be chosen carefully to minimize errors.

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