Development of digital oil for technological innovation in petroleum engineering*

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Abstract: Engineering science largely relies on a fundamental understanding on the structure-property relationships at various spatial and time scales. Digital oil is a molecular model of crude oil that is represented by multiple representative molecules created based on analytical data. This concept was proposed by our group in 2014 inspired by the concepts of digital field and digital rock, which emerged, historically, in the oil industry as critical technical revolutions. For five years, my colleagues and I have been working on digital oil and constructed two types of light crude oil as well as two types of heavy crude oil models with one being oil sand bitumen. So far, the applications include: (1) predicting asphaltene precipitation, (2) better solutions to asphaltene problems, and (3) heavy oil development. For heavy oil, we developed the method for constructing molecular models of saturates and aromatics. To predict phase behavior, we are working on a coarse-grained digital oil model. Digital oil builds a bridge between basic petroleum chemistry and engineering via molecular simulation techniques. We believe that this technique will be widely used for solving problems in both upstream and downstream in oil industry.

Keywords: digital oil, molecular model, molecular dynamics simulation, asphaltene, heavy oil, enhanced oil recovery

1. Introduction

In oil and gas industry, the method to construct “digital field” (i.e., a geological reservoir model) has been established in 1990s with the achievement of 3D seismology (see a review, e.g., Matsuoka 2013). It became practical to have 3D images of sedimentary basin and oil reservoirs (with necessary logging information about the sediments). The digital rock has been developed in 2000s with the help of X-ray computed tomography (CT) and focused ion beam-scanning electron microscope (FIB-SEM), as well as some other tools (Akai et al., 2016). It is possible to understand the bulk and surface chemistry of minerals, and also the pore structure (Akai et al., 2016). Furthermore, it has been combined with fluid dynamics simulation such as lattice Boltzmann method (LBM) and pore event simulation to study the displacement mechanism for two-phase flow in porous media (Yamabe et al., 2015). Digital oil is a molecular model for crude oil that is represented by multiple representative molecules created based on analytical data. We proposed this concept at the SPE Applied Technology Workshop on “Nanotechnology and Nanogeosciences in Oil and Gas Industry” held in Kyoto in 2014 (Tagami et al., 2014). With the full molecular model of the crude, it is easy to study the crude fluid properties, such as density, viscosity, diffusion coefficient, heat capacity, thermal conductivity, mechanical properties, and phase behavior (Tagami et al., 2014; Hibi et al., 2014; Sugiyama et al., 2018; Iwase et al., 2018a; Iwase et al., 2018b; Iwase et al., 2019; Huo et al., 2019). It also enables the molecular-scale studies on asphaltene aggregation, deposition, and precipitation, wax precipitation, wettability alternation, emulsions, and chemicals for enhanced oil recovery (EOR). Fig. 1 shows a schematic diagram for the proposal of digital oil along with digital rock and digital field, and the role of digital oil in multiscale simulations of the complicated behaviors of complex materials in oil field. In this paper, I’ll explain how we can benefit from the petroleum chemistry achievement and construct digital oil models for the applications in petroleum engineering.

In the past semicentury, petroleum chemistry has made a substantial advancement (Mullins 2007; Speight 2014). The molecular structures of asphaltenes have been revealed by atomic force microscopy (AFM) and molecular orbital...
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imaging using scanning tunneling microscopy (STM) (Schuler et al., 2015). Efforts have been made to distinguish the heteroatoms in aromatic molecules for AFM imaging (Zahl and Zhang 2019). The structures and relative abundances of petroleum acids and bases with oxygen and nitrogen heteroatoms have been long recognized (Cyr and Strausz 1984; Frakman et al., 1990; Lochte 1952; Richter et al., 1952; Yamamoto et al., 1991; Yamamoto and Taguchi 2000). The structures and relative abundances of petroleum acids and bases with oxygen and nitrogen heteroatoms have been long recognized (Cyr and Strausz 1984; Frakman et al., 1990; Lochte 1952; Richter et al., 1952; Yamamoto et al., 1991; Yamamoto and Taguchi 2000). The sulfur compounds can be isolated and analyzed by infrared spectra after oxidizing sulfides to sulfoxides (Payzant et al., 1989; Gray et al., 1995). Direct determination and quantification of sulfur compounds in petroleum can be made possible by K-edge X-Ray absorption spectra, X-Ray photoelectron spectroscopy, and X-ray fluorescence sulfur-in-oil analyzer (Spiro et al., 1984; George and Gorbaty 1989; Kelemen et al., 1990; Gorbaty et al., 1990; Waldo et al., 1991; Shirai and Sugawara 1999; George et al., 2014). The chemical structure of different fractions of crude oils has been analyzed by gas chromatography (GC), GC-mass spectrometry (MS), and $^1$H and $^{13}$C NMR spectra (Selucky et al., 1977; Suzuki et al., 1982; Strausz et al., 2010; Strausz et al., 2011). The asphaltene structure has been better defined being the island molecular architecture dominant (Yen et al., 1961; Dickie and Yen 1967; Groenzin and Mullins 2000; Mullins 2010; Sabbah et al., 2011; Mullins et al., 2012). This majorly resulted from a consensus on the molecular weight of the asphaltene molecules because of molecular diffusion measurement by time-resolved fluorescence depolarization experiment (Groenzin and Mullins 2000) and early studies based on X-ray diffraction (Yen et al., 1961). The ultrahigh resolution Fourier transform ion cyclotron resonance MS (FT-ICR MS) has recently revealed that a crude oil may contain more than 400,000 types of molecules, which differ by elemental compositions (Marshall and Rodgers 2004; 2008). By considering the chemically distinct constituents (such as isomers), it may reach a countless number. This has led to a well-known conception of petroleomics (Marshall and Rodgers 2004; 2008), which stands for a detailed characterization of petroleum at the molecular level.

Owing to the development of computational technology, molecular models and molecular dynamics (MD) simulations are now widely used in the studies related to petroleum engineering (van Buuren et al., 1993; Murgich et al., 1999; Jang et al., 2004; Kunieda et al., 2010; Castello et al., 2012; Aquing et al., 2012; Makimura et al., 2012; Mikami et al., 2013; Yang et al., 2015; Kobayashi et al., 2017; Liang et al., 2017; Sugiyama et al., 2018; Iwase et al., 2018; Huo et al., 2019; Mizuhara et al., 2019). One of the advantages of MD simulations is to provide insights that cannot be extracted from experiments alone. In these MD simulations, an oil model is needed. In early studies, researchers used pure hydrocarbon as an oil phase because of their simplicity (van Buuren et al., 1993; Jang et al., 2004). More recently, Kunieda et al., (2010) employed a simple light oil containing eight...
kinds of hydrocarbons including paraffin, naphthenic, and aromatic molecules. Theoretically, a molecular model of crude oil must contain all the components of that crude, however, it is impossible to detect all of these, especially, for a heavy crude (Marshall and Rodgers 2004; 2008). Thus, molecular models need to be appropriately simplified. One approach is to use a mixture of representative molecules based on measurements of the whole sample (Boek et al., 2009; Sheremata et al., 2004). Digital oil is a molecular model of crude oil, which is represented as a mixture of representative molecules of respect fractions (Sugiyama et al., 2018; Iwase et al., 2018). Because the representative molecules were generated to reproduce all the available experimental data, such as elemental analysis, molecular weight measurement and $^1$H and $^{13}$C NMR experiments, all the components need not be identified when the separation is unworkable. To compare with the concept of petroleomics, digital oil model provides mixture models imitating distributions of samples based on analytical data, rather than to identify all the molecules in crude oil. In another word, petroleomics strengthens the importance of identification (Marshall and Rodgers 2004; 2008). The digital oil emphasizes the quantification and molecular-scale modeling with some necessary simplifications. Notwithstanding the simplifications, digital oil can include those already identified molecules (Sugiyama et al., 2018). Once we construct a digital oil, we can analyze both its macroscopic properties and microscopic phenomena under any thermodynamic conditions using MD simulations. In the following sections, I’ll explain a couple of examples and describe our future work.

2. Examples

2.1 Construction of digital oil and evaluation of crude oil properties

So far, we have constructed two types of light crude oil and two types of heavy crude oil with one being oil sand bitumen (Tagami et al., 2014; Hibi et al., 2014; Sugiyama et al., 2018; Iwase et al., 2018a; Iwase et al., 2018b; Iwase et al., 2019; Huo et al., 2019). As shown in Fig. 2, the overall procedure includes separation of crude oil, analysis of each fraction, and construction of the molecular models.

For the light crude oil, the first step of separation of the sample oil was extracting the asphaltenes by the heptane extraction process. Here, asphaltenes are defined as oil components insoluble in heptane but soluble in toluene. The components except for asphaltenes are called maltenes. Detailed separation of asphaltenes were described by Sugiyama et al., (2018). After the separation of asphaltenes, the maltenes were separated into the light and heavy fractions, of which the boiling points were below and above 500°C, respectively. The gas and light fractions were analyzed by GC-MS and GC-flame ionization detector (GC-FID) (Fig. 2 (a)). GC is one of separation techniques applied for a volatile sample. MS ionizes a component and determines the kind of the component from a distribution of fragments by comparing with reference data (Babushok et al., 2007). FID can quantitatively detect a component in accordance with carbon atoms and determine mole fractions of those components, comparing with the data measured by a MS detector. Hundreds of kinds of molecules, including normal alkanes, isoalkanes, naphthenes, alkylbenzenes, and polyaromatics (with a maximum of three aromatic rings), were directly identified for one light crude oil. The heavy fraction and asphaltenes were analyzed by elemental analysis, molecular weight measurement with gel permeation chromatography, and $^1$H and $^{13}$C nuclear magnetic resonance spectroscopy, and represented by quantitative molecular representation (QMR) (Boek et al., 2009), which provides a mixture model imitating distributions of crude oil heavy fraction and asphaltene samples, respectively.

For the heavy crude oil, crude oil was separated into four fractions: saturates, aromatics, resins, and asphaltene (SARA) (Fig. 2 (b)). In the SARA separation, the heavy crude oil was, at first, diluted with heptane and separated into the precipitated asphaltenes, and the dissolved maltenes in heptane by filtration and reflux. Moreover, the saturates, aromatics and resins were extracted from the maltenes by alumina column with heptane, toluene and methanol-toluene solvents. The digital oil was constructed as a mixture of representative molecules of saturates, aromatics, resins, asphaltene, and lost components (low boiling-point compounds vaporized during drying). It is worthy to mention that SARA analysis was introduced in order to solve problems...
that we could not identify the light fractions of heavy crude oils by combination of GC-MS and GC-FID methods (Iwase et al., 2018), although the situation remained the same for saturates and aromatics: that is, we could not identify the saturates and aromatics of heavy crude oils by GC-FID methods. Consequently, we must use QMR for all the fractions. The additional merit of SARA analysis is that we can get the molecular models explicitly for resin fractions, which have not been investigated in detail. Note that the SARA separation should not be applied to light crude oil because some components in the light oil can be largely lost in the column chromatography. However, if we wish to explicitly understand the molecular structure of resin fractions, other than just heavy fractions, one may consider this recipe.

The procedure of construction of QMR model is mainly divided into the two processes: the generation process and optimization process (Fig. 3). A molecule can be described by the following 6 parameters on attributes: (1) a number of unit sheets (US), (2) a number of aromatic rings per US, (3) a number of naphthenic rings per US, (4) aromatic carbons linking with an alkyl chain, (5) naphthenic carbons linking with an alkyl chain and (6) length of chains. Here, US is a lump of aromatic and naphthenic rings. In the generation process, the 6 parameters are randomly sampled from each probability distribution function by the Monte Carlo algorithm. Then, building blocks are connected based on the 6 parameters. Finally, one molecule is constructed. With repetition of the sampling and the connecting, N molecules are generated in the generation process. Then, in the optimization process, the objective deviation \( F \), represented by Eq. (1), is calculated on many sets of \( M \) molecules within the \( N \) molecules.

\[
F = \sum_{i=1}^{7} \left( \frac{\hat{\mu}_i - \bar{\mu}_i}{\sigma_i} \right)^2 + \frac{1}{11} \sum_{i=8}^{18} \left( \frac{\hat{\mu}_i - \bar{\mu}_i}{\sigma_i} \right)^2
\]

Where

\( \hat{\mu}_i \): experimental value

\( \mu_i \): calculated value for each molecule

\( \sigma \): experimental error

\( \hat{\mu} \): calculated value for a mixture model

\( M \): number of molecules

\( x \): mole fraction

\( \hat{\mu}_n \): calculated value for each molecular model

\( \mu' \): experimental value

\( M' \): number of molecules

\( x' \): mole fraction

\( \hat{\mu}'_n \): calculated value for each molecular model

Fig. 3 QMR method with two steps

(1) generation; (2) optimization.

In Eqs. (1) and (2), \( i \) is an index of property, \( \mu_i \) is a measured value of property \( i \), \( \sigma_i \) is an estimated error of \( \mu_i \), \( \mu'_i \) is a calculated value of properties from a certain set of \( M \) molecules, \( j \) is an index of molecules, \( x_j \) is mole fraction of molecule \( j \), \( \mu'_i,j \) is a value of property \( i \) of molecule \( j \). Values in the first term in Eq. (1) (\( i = 1 \) to 7) are related to number average molecular weight and elemental composition. Values in the second term in Eq. (1) (\( i = 8 \) to 18) are relevant to carbon types estimated from the NMR spectroscopy (Fig. 4). Due to low accuracy of NMR data, the coefficient (1/11) is attached to the second term. In this study, a sequential optimization scheme was conducted. That is, firstly, the molecule giving the lowest \( F \) value in the \( N \) molecules is selected. Then, \( F \) values of all combinations between the selected molecule and the other molecules are calculated and the set giving the lowest \( F \) value is selected. The process of adding molecules continues until \( M \) molecules are selected, for which \( F \) value converges. For the generation, normally, 4,000 molecules are generated; for optimization, one QMR set includes 4–6 molecules. The building blocks can be added by user based on available experimental data (Cyr and Strausz 1984; Frakman et al., 1990; Lochte 1952; Richter et al., 1952; Yamamoto et al., 1991; Yamamoto and Taguchi 2000; Payzant et al., 1989; Gray et al., 1995).

For asphaltenes, resins, and heavy fractions, QMR process was conducted by Asphaltene Factory simulation software developed by Boek et al., (2009). To enable the QMR method to be applicable to saturates, we extended it with two developments (Iwase et al., 2018a): the first was the generation of nonaromatic molecules by a new algorithm that can generate a more branched structure by separating the chain bonding into main and subsidiary processes; the second was that the molecular mass distribution of the model could be fitted to that obtained from GC distillation (GCD).
experiments. The latter was also applied to aromatics.

Fig. 5 shows model of asphaltenes for a light crude oil. The averages of the US number, number of aromatic rings per US, number of naphthenic rings per US, and chain length of asphaltene are 1.4, 8.7, 1.9 and 4.3, respectively. Numbers of aromatic rings per US on all the asphaltene molecular models are within the range from 7 to 10, which is consistent with previous studies (Mullins 2010; Mullins et al., 2012). In

| No. | Property       | No. | Property (%) mol C |
|-----|----------------|-----|--------------------|
| 1   | $M_n$          | 8   | $Q_1$: Alkyl-substituted aromatic quaternary C |
| 2   | C (wt %)       | 9   | $Q_2$: Bridgehead aromatic quaternary C |
| 3   | H (wt %)       | 10  | $C_1$: Aromatic CH beside $Q_2$ |
| 4   | N (wt %)       | 11  | $C_2$: Aromatic CH except $C_1$ |
| 5   | S (wt %)       | 12  | Other aliphatic CH |
| 6   | O (wt %)       | 13  | Total $\alpha$-CH |
| 7   | V (ppm)        | 14  | $\beta$-CH |
|     |                | 15  | Chain CH |
|     |                | 16  | Aliphatic CH |
|     |                | 17  | Naphthenic CH |
|     |                | 18  | $\gamma$-CH |

Fig. 4 Parameters in QMR method along with schematic diagram of carbon structures

Fig. 5 Model of the asphaltenes of light crude oil
Reproduced with permission from Sugiyama et al., (2018).
addition, we observed that an island-type molecule (Sugiyama et al., 2018; Tagami et al., 2014; Hibi et al., 2014; Huo et al., 2019), namely, a molecule with a single US, is dominant, as proposed previously (Mullins 2010; Sabbah et al., 2011; Mullins et al., 2012); in our case, the average US number is 1.0–1.4 for four different crude oils. In an oil field, which suffers from serious emulsion problems, we show that the asphaltene is nitrogen-rich, and the asphaltene molecule contains pyridine-type structure (Hibi et al., 2014; Murata et al., 2016). The calculated adsorption free energy (−6.9 kJ/mol) of this asphaltene at oil-water interface was found to be four times higher than that of asphaltene containing no heteroatoms (−1.5 kJ/mol) (Mizuhara et al., 2019), which shows our efforts are helpful and relevant to engineering applications. Although the asphaltene structure has been better defined being the island molecular architecture dominant, there are also possibilities to have asphaltene molecules with 2 or more polycyclic aromatic hydrocarbon sheets (i.e. archipelago model) (Dickie and Yen 1967; Mullins 2010; Mullins et al., 2012). Besides, there are two (not one) distinct nano-colloidal species observed (Eyssautier et al., 2011). Previous AFM measurement confirmed that a single aromatic core with peripheral alkane chains is the dominant asphaltene architecture (Schuler et al., 2015). However, it also showed that many asphaltenes (under inspection) exhibit a significantly large size than those in Yen-Mullins model (Schuler et al., 2015). To this end, our mixture model of asphaltenes could contribute further studies on the above scientific debates by a variety of molecular structures in one set.

To confirm the validity of the digital oil, density was calculated for all the four digital oil models by MD simulations. Fig. 6 (a) shows one example for a light crude oil, which show good agreement with experimental data. So far, the calculated density reproduced experimental data very well with deviations within 2% for heavy crude oils, and 5% for light crude oils, which indicates our digital oil model is reasonable for further applications. Fig. 6 (b) shows the calculated results of viscosity from the equilibrium MD (EMD) and non-equilibrium MD (NEMD) simulations for a light crude oil (Sugiyama et al., 2018). Here, the EMD is based on the Einstein equation method and NEMD is based on the Navier-Stokes equation method. The calculated results show a systematic deviation of ~60%, and hence were corrected by multiplying a scale factor. Although the scale factor did not have a physical meaning, the corrected viscosities were in good agreement with the experimental results in the range between 3.0 and 29.5 MPa. Furthermore, the calculated viscosity for a heavy crude oil showed a systematic deviation of ~50% (Iwase et al., 2018). These facts indicate that we can tolerate such deviations, and perform extensive simulations with the digital oil model, when a few experimental data are available for calibration.

2.2 Prediction of asphaltene precipitation and finding solutions for asphaltene deposition problems

For a long time, a simple cubic equation of state (EOS) method, such as the Peng-Robinson EOS (PR-EOS) and Soave-Redlich-Kwong EOS (SRK-EOS), has been widely used in oil and gas industry for their accuracy and simplicity (Pedersen and Christensen, 2006). However, they can’t consider asphaltene problems easily. Recently, a cubic-plus-association equation of state (CPA-EOS) was proposed to study asphaltene precipitation, where the PR-EOS model is combined with the Wertheim association formulation (Li and Firoozabadi 2010a; 2010b). This model has been employed to PVT simulations because of its simplicity. It enables us to determine temperature and pressure conditions for asphaltene precipitation by drawing phase envelope of a liquid asphaltene phase. In CPA-EOS, the excess Helmholtz free energy is composed of physical contribution, which is

![Fig. 6](image_url) Comparison of calculated density (a) and viscosity (b) as a function of pressure with measured data Reproduced with permission from Sugiyama et al., (2018). Note, the green circle at around 6 MPa is for a mixture of vapor and liquid. For the pressure lower than 16.3 MPa, flash calculation was performed using PVTsim nova (Calsep, Denmark) to determine the components in the liquid phase.
represented by PR-EOS, and the association contribution, which is represented as the following formula:

\[
\frac{A_{\text{assoc}}^{\text{TR}}}{nRT} = N_A \frac{1}{\alpha} \ln \chi_A + \frac{1}{2} \left( 1 - \frac{\chi_A}{\alpha} \right) + N_R \frac{1}{\alpha} \ln \chi_R + \frac{1}{2} \left( 1 - \frac{\chi_R}{\alpha} \right)
\]  

(3)

where \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( n \) is the total number of moles. The subscripts ‘A’ and ‘R’ denote asphaltenes and resins, respectively. \( N_A \) and \( N_R \) are the numbers of association sites for asphaltenes and resins, respectively. \( \chi_A \) and \( \chi_R \) are the mole fractions of asphaltenes and resins, respectively. \( \chi_A \) and \( \chi_R \) are the molefractions of asphaltenes and resins, which are in the lean phase, namely not bonded at the association sites. \( \chi_A \) and \( \chi_R \) are calculated iteratively as follows:

\[
\chi_A = \frac{1}{1 + \rho_{\text{mol}} N_A \chi_A \Delta^{\text{AA}} + \rho_{\text{mol}} N_R \chi_R \Delta^{\text{AR}}}
\]  

(4)

\[
\chi_R = \frac{1}{1 + \rho_{\text{mol}} N_A \chi_A \Delta^{\text{RA}} + \rho_{\text{mol}} N_R \chi_R \Delta^{\text{RR}}}
\]  

(5)

where \( \rho_{\text{mol}} \) is molar density of the mixture, and \( \Delta^{\text{AA}} \) or \( \Delta^{\text{RR}} \) is represented by:

\[
\Delta^{ij} = g \kappa_i b_{ij} \left[ \exp \left( \frac{\epsilon^{ij}}{k_b T} \right) - 1 \right] (i = A \text{ and } j = A \text{ or } R)
\]  

(6)

where \( b \) is volume parameter of the mixture and \( b_{ij} = \frac{b_i + b_j}{2} \),

\( g \) is the contact value of the radial distribution function of the hard-spheres, \( k_b \) is Boltzmann constant, \( \kappa_i \) is the association volume parameter, and \( \epsilon^{ij} \) is the association energy parameter. The association energy parameter includes self-association energy \( \epsilon^{AA} \) and cross-association energy \( \epsilon^{AR} \), which are crucial to describe the asphaltene precipitation. In CPA-EOS, the self-association energy is set to be a constant value by no means to be concrete, while the cross-association energy is an adjustable parameter. Such way of setting the parameters stems from the difficulty to evaluate the association energy by the currently available experiments. In summary, CPA-EOS is very effective when modeling the asphaltene precipitation through phase equilibrium calculations, but we could not input the association energies confidently. Thus, one of our major tasks was to calculate the association energies as reliable as possible, for the application of CPA-EOS to predict the asphaltene precipitation risk.

Fig. 7 shows a flowchart of our proposed research scheme with digital oil. By using analytical experiments of crude oil for a target reservoir, we first construct a realistic crude oil model (i.e., digital oil), which contains many kinds of molecular models. Then, we employ asphaltene and digital oil models to calculate the asphaltene self- and cross-association energies. After that, we can apply the calculated association energies into CPA-EOS model to calculate the phase equilibria for prediction of asphaltene precipitation risk. We can also use digital oil to study the asphaltene aggregation status by combining with the injected gas, when the natural gas- or CO\(_2\)-EOR is being applied. In previous study, we calculated asphaltene self-association energy (Sugiyama et al., 2018) in the digital oil at the reservoir condition, from the potential of mean force (PMF) calculations using MD simulation with the umbrella sampling method. The calculated value is consistent with reported ones used in phase equilibrium calculation. As mentioned above, such calculated association energy can be used with CPA-EOS to predict asphaltene precipitation risks during an EOR process (Sugiyama et al., 2018; Hibi et al., 2014).

In addition, we developed a method to find better solvent for asphaltene deposition problems based on association energies of asphaltenes in proposed solvents (Hibi et al., 2015; Murata et al., 2016). We calculated asphaltene-asphaltene association energies in seven different liquids: heptane, toluene, benzene, xylene, isopropyl alcohol (IPA), an azetrope mixture of toluene and IPA, and a ternary azetrope mixture of water, toluene, and IPA. As anticipated, aromatics (toluene, benzene, and xylene) presents much lower association energies of asphaltene in absolute value than that in heptane, among which the xylene shows the lowest value. IPA presents two minimum wells with a much high association energy in absolute value. These two minimum wells are flattened by mixing with toluene, and consequently the mixture presents a comparable association energy to xylene. The ternary mixture provides the lowest association energy of the solvents that we studied. Therefore, it can be more effective solvent for asphaltene (Fig. 8). This is because the solvent power can be tuned to better fit the specific asphaltenes by adding alcohol and water. Our study provides a systematic, perhaps, also economical method to design asphaltene solvents for a specific well.
2.3 Heavy oil development

Efficient recovery of heavy oil, which includes extra heavy oil and bitumen, has been attractive with the depletion of conventional light oil reserves and expansion of energy demands (Alboudwarej et al., 2006; Curtis et al., 2002). The major difficulty is that heavy oil and bitumen are partially or completely immobile under reservoir conditions due to its extremely high viscosity and heavier molecular compositions. EOR is therefore an essential technique for heavy-oil recovery, even at the early development stage. Steam-assisted gravity drainage (SAGD) is the most widely commercialized process for bitumen and heavy-oil recovery. SAGD takes advantages of the strong temperature dependency of bitumen viscosity. Since steam gives huge latent heat to heavy crude oil when it is condensed to liquid water, the viscosity of the heavy oil is much reduced, and the heavy oil become movable to the production well. In the SAGD process, the steam injected from a horizontal well forms a steam chamber. The heated bitumen drains under gravity towards the production well, which is located at several meters below the injection well. This process offers a couple of key advantages, including high ultimate recovery and stable oil production rates (Butler 1991). However, high energy demands and environmental concerns, such as high levels of carbon dioxide (CO₂) emission and large quantities of fresh water, have necessitated emerging alternative processes (Imai et al., 2019).

Solvent-aided SAGD (SA-SAGD) has been proposed as an alternative to improve the efficiency of SAGD. In SA-SAGD, a small amount of hydrocarbon solvent is co-injected with steam to further reduce the viscosity of bitumen near the chamber edge. This process requires a smaller amount of steam to recover the same amount of bitumen and can exhibit higher oil production rate than SAGD, which, according to Imperial Oil, can reduce water use and CO₂ emission about 25% (Zborowski and Writer 2019). Vapor extraction (VAPEX), one of the cold-production processes, has also been proposed as an alternative for heavy-oil recovery. In VAPEX, vaporized solvents are injected instead of steam, which dissolve into the oil, diluting the oil and decreasing its viscosity. Compared to liquid solvents, vaporized solvents provide a higher driving force for the gravity drainage of heavy oil and are easily recoverable for recycling (Upreti et al., 2007).

In both SA-SAGD and VAPEX processes, selecting the appropriate solvent for a reservoir is the most essential task because the effectiveness of solvents varies depending on the oil field. Oil viscosity is a key factor for evaluating the effectiveness of these different solvents. For heavy oils, characterizing viscosity behavior is especially important because even small changes can have large effects on production rates and recoverable oil volumes. The production rate of SA-SAGD and VAPEX is also strongly dependent on the oil viscosity reduction, which in turn depends on the dissolution of the solvent into the heavy oil mainly through molecular diffusion. Therefore, diffusion coefficient of the solvent is another key factor. Molecular diffusion is caused by the concentration gradients of each component in oil and gas phases. This diffusion effect is especially important in the gas injection process because the concentration gradients easily occur near the injection zone in this process. Molecular diffusion coefficients into oils have been characterized in several ways (Ohata et al., 2015; Imai et al., 2019). Ohata et al., (2015) estimated the molecular diffusion coefficients from a combination of experimental data using PVT cell and simulation matching. Imai et al., (2019) estimated the molecular diffusion coefficients from experimental data using X-ray CT. In addition, swelling factor, defined as the ratio of the volume of the oil–solvent mixture to the original oil volume, can also be an important parameter. Oil swelling is an expansion in oil volume when the solvent is injected into the reservoir fluid, which can result in enhancing the oil recovery by mobilizing residual oil and increasing the oil saturation and relative permeability. To grasp these properties leads to selecting the effective solvents, field design of the recovery processes, and understanding the oil-recovery mechanisms. These properties are determined based on interactions between the oil components and the solvent. Therefore, it

![Fig. 8 Calculated association energy of asphaltenes in seven liquids](image)

Adapted with permission from Hibi et al., (2015).
is necessary to understand the oil components and their property changes when various solvents are added.

In one of our studies, a heavy crude oil sample was used as a target oil to study the EOR processes. In this oil field, there are two different reservoirs: “shallow” and “deep”. The heavy crude oil used in this study was obtained from the shallow reservoir. The deep one is a gas condensate reservoir. This oil field has not yet been in production, so several EOR processes are now being studied extensively in experiments and simulations. Natural gas (methane) injection is considered as a candidate because it can be easily recovered from the deep reservoir. In addition, this oil field is located near a carbon dioxide capture and storage (CCS) site, so CO$_2$ injection can also be a promising candidate. To evaluate the effectiveness of various solvents for heavy crude oil, we calculated the oil property changes when different solvents were added into the digital oil (Iwase et al., 2019). First, we compared methane and carbon dioxide (CO$_2$) (Fig. 9). The results indicated that CO$_2$ had the higher effectiveness in terms of oil-viscosity reduction, oil swelling, and diffusion into the oil. Second, we evaluated the effectiveness of eleven different solvents. It was found that ethane had the greatest influence on oil-viscosity reduction and oil swelling, and CO$_2$ had the highest diffusion coefficient. From these results, ethane and CO$_2$ turned out to be the appropriate solvents for this crude oil (Iwase et al., 2019).

### 3. Summary and future work

In summary, we have constructed digital oil for four crude oils, which show reasonable agreement with experiments. For the study of crude oil, chemical composition requires both identity and quality of each component. Digital oil has found a compromise between identifying countless species in a crude oil and an accurate crude oil model by imitating all available analytical data. We applied the digital oil model for investigation of crude oil properties, heavy oil development, prediction and a better solution for asphaltene deposition problems. We now use the digital oil technique: (1) to solve asphaltene deposition problems in production system linked with water (such as emulsion problems), (2) to find a better strategy in SA-SAGD processes for oil sand bitumen, (3) to understand the nonlinear bimodal phenomenon on the concentration dependence of mutual diffusion coefficients for solvent and bitumen mixtures (that is, the diffusion coefficient as function of concentration shows two peaks) (Imai et al., 2019), and (4) to understand molecular behavior of surfactants (such as alkyl benzene sulfonate) at the oil-water interface for finding effective surfactants in EOR.

When we use the digital oil model to evaluate the crude oil properties at reservoir conditions, it was necessary to combine EOS model to calculate liquid components (Sugiyama et al., 2018; Iwase et al., 2019). Fondly, it will be of dream to predict the phase behavior of crude oil in the reservoir by only MD simulations (without EOS model). A coarse-grained digital oil model was chosen as our next step to realize it. The idea is to use coarse-grained force field (Herdes et al., 2015) to describe our digital oil. The coarse-grained statistical associating fluid theory (SAFT) force field parameters are based on Mie potential, which are deduced from cubic EOS. In addition, a complicated molecule can be described with only a few beads. So, it has advantage to simulate the vapor-liquid phase behavior, which requires a large-size simulation system typically about 100 nm in length. In terms of computational time, it needs about 1/10 of that using a full-atom potential. For the light condensate mixture, the bubble point pressure predictions show only a deviation of 0.92% (Herdes et al., 2015). Fig. 10 shows an example

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**Fig. 9** Calculated viscosities for digital oil-CH$_4$ and digital oil-CO$_2$ mixtures

Reproduced with permission from Iwase et al., (2019).

**Fig. 10** Determination of bubble point pressure for N$_2$/nC$_{10}$H$_{22}$ System

Note: box size (alone Z) times cross-section area (in x-y plane) is the system volume. The blue data points are in single liquid phase with a low compressibility; the orange data points are in two-phase regime. The crossing point of two lines is determined as the bubble point pressure.
of N₂/n-C₆H₁₃ system on how to determine the bubble-point pressure with MD simulations. The result is still preliminary, but it shows the potential. One of our future works will, thus, be to create coarse-grained digital oil model to calculate the vapor-liquid equilibrium directly.

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石油工学における技術革新のための
デジタルオイルの開発

梁 云峰

デジタルオイルは、分析データに基づいて作成された複数の代表的な分子によって表現される原油に対する分子モデルである。2014年に京都で開催されたSPE応用技術ワークショップでこの概念を提案し、それ以来、筆者はデジタルオイルの石油工学への利用のための研究開発に取り組んできた。デジタルオイルという概念は石油工学においては、(1) 生産活動に伴う貯留層の温度圧力変化に対するアスファルテン沈殿の予測、(2) アスファルテン凝固が起こり易い種々の問題に対する解決法の提案、(3) オイルサンプル中の重質油に対する効率的な生産手法の検討への利用が考えられる。本発表ではこれらに関して、筆者のグループがこれまでに行ってきた研究について述べる。また、貯留層内における原油相挙動の予測のための複合化デジタルオイルモデル作成に関する研究など、現在取り組んでいる研究について紹介する。