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Prediction of Asphaltene Precipitation: Learning from Data at Different Conditions

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Asphaltene precipitation affects enhanced oil recovery processes through the mechanism of wettability alteration and blockage. Asphaltene precipitation is very sensitive to the reservoir conditions and fluid properties, such as pressure, temperature, dilution ratio, and injected fluid molecular weight. A Bayesian belief network (BBN) was used in this study as an artificial intelligence modeling tool to investigate the effect of different variables/parameters on asphaltene precipitation. The predicted results from the BBN model were compared to the experimental precipitation data obtained using high-resolution images captured in a high-pressure cell and processed by image analysis software. The cell accessories facilitate *in situ* visual monitoring of nuclei growth of asphaltene at high pressures and specified temperatures. The average relative absolute deviation between the model predictions and the experimental data was found to be less than 4.6%. Burst of nucleation or the onset of asphaltene precipitation was also determined at different conditions directly by the developed BBN model. A comparison between the prediction of this model and the alternatives showed that the BBN model predicts asphaltene precipitation more accurately and covers a wider range of affected variables/parameters.

1. Introduction

Gas injection is widely used as an enhanced oil recovery (EOR) process in the petroleum industry. Gas injection would maintain the reservoir pressure and increase the sweeping efficiency at high-pressure conditions through the immiscible or miscible displacements. Gas injection may encounter asphaltene precipitation through which a sticky, asphalt-like substance plugs the reservoir and production equipment.[1] On the basis of solubility, asphaltene is defined as that fraction of petroleum that is insoluble in *n*-alkanes and completely soluble in aromatics, such as toluene and benzene.[2] The extent of asphaltene precipitation depends upon the composition of the crude oil, the precipitating agent, and the pressure and temperature of the reservoir. Asphaltene precipitation may change the formation wettability and, hence, reduce the sweep efficiency of the reservoir.[3] Therefore, the prediction of asphaltene precipitation will be essential for solvent injection into the oil reservoir as a means to prevent plugging.

Over the last 2 decades, many theoretical and experimental studies have been reported in the literature, and great achievement has been gained in recent years.[4−20] Models developed for prediction of asphaltene precipitation are either thermodynamic

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(1) Vasquez, D.; Mansoori, G. A. Identification and measurement of petroleum precipitates. *J. Pet. Sci. Eng*. **2000**, *26*, 49–55.
(2) Speight, J. G. *Fuel Science and Technology Handbook*; Marcel Dekker: New York, 1990; ISBN: 0-824-78171-6.
(3) Lichaa, P. M.; Herrera, L. Electrical and other effects related to the formation and prevention of asphaltenes deposition. *SPE J*. **1975**, *5304*, 107–125.
(4) Mofidi, M.; Edalat, M. A simplified thermodynamic modeling procedure for predicting asphaltene precipitation. *Fuel* **2006**, *85*, 2616–2621.
(5) Li, Z.; Firoozabadi, A. Modeling asphaltene precipitation by *n*-alkanes from heavy oils and bitumens using cubic-plus-association equation of state. *Energy Fuels* **2010**, *24* (2), 1106–1113.
(6) Alboudwarej, H.; Akbarzadeh, K.; Beck, J.; Svrcek, W. Y.; Yarranton., H. W. Regular solution model for asphaltene precipitation from bitumens and solvents. *AIChE J*. **2003**, *49*, 2948–2956.
(7) Speight, J. G.; Wernick, D. L.; Gould, K. A.; Overfield, R. E.; Rao, B. M. L.; Savage, D. W. Molecular weight and association of asphaltenes: A critical review. *Rev. Inst. Fr. Pet*. **1985**, *40*, 51–61.
(8) Mozaffarian, M.; Dabir, B.; Sohrabi, M.; Rassamanda, H.; Sahimi, M. Asphalt flocculation and deposition IV. Dynamic evolution of the heavy organic compounds. *Fuel* **1990**, *76*, 1479–1490.
(9) Andersen, S. I.; Speight, J. Thermodynamic models for asphaltene solubility and precipitation. *J. Pet. Sci. Eng*. **1999**, *22*, 53–66.
(10) Correra, S.; Donaggio, F. OCCAM: Onset-constrained colloidal asphaltene model. Presented at the SPE International Symposium on Formation Damage, Lafayette, LA, Feb, 2000; SPE Technical Paper 58724.
(11) Akbarzadeh, K.; Ayatollahi, S.; Moshfeghian, M.; Alboudwarej, H.; Yarranton, H. W. Estimation of SARA fraction properties with the SRK EOS. *J. Can. Pet. Technol*. **2004**, *43*, 31–39.
(12) Moschopedis, S. E.; Speight, J. G. Investigation of hydrogen bonding by oxygen functions in Athabasca bitumen. *Fuel* **1976**, *55* (3), 187–192.
(13) Dabir, B.; Nemati, M.; Mehrabi, A. R.; Rassamanda, H.; Sahimi, M. Asphalt flocculation and deposition. III. The molecular weight distribution. *Fuel* **1996**, *75*, 1633–1645.
(14) Andersen, S. I.; Birdi, K. S. Aggregation of asphaltenes as determined by calorimetry. *J. Colloid Interface Sci*. **1991**, *142* (2), 497–502.
(15) Sheu, E. Y.; DeTar, M. M.; Storm, D. A.; DeCanio, S. J. Aggregation and kinetics of asphaltenes in organic solvents. *Fuel* **1992**, *71* (3), 299–302.
(16) Sheu, E. Y.; Sinha, K. S.; Overfield, R. E. Polydispersity analysis of asphaltene solutions in toluene. *J. Colloid Interface Sci*. **1992**, *153*, 399–410.
(17) Pedersen, K. S.; Fredenslund, A.; Thomassen, P. *Properties of Oils and Natural Gases*; Gulf Publishing Company: Houston, TX, 1989; ISBN: 0-872-01588-2.
(18) Rassamdana, H.; Sahimi, M. Asphalt flocculation and deposition: II. Formation and growth of fractal aggregates. *AIChE J*. **1996**, *42* (12), 3318–3332.
(19) Rassamdana, H.; Dabir, B.; Nematy, M.; Farhani, M.; Sahimi, M. Asphalt flocculation and deposition: I. The onset of precipitation. *AIChE J*. **1996**, *42*, 10–22.

or scaling models. Thermodynamic models are based on the asphaltene properties, while the foundation of scaling models is the aggregation/gelation phenomena. Thermodynamic models are divided into three groups: statistical thermodynamic, continuous thermodynamic, and molecular thermodynamic.[4] Parameter tuning of the first two models requires a great amount of experimental data. However, the third one includes less adjustable parameters.[4,5] Instead, it requires information on the density, molecular weight, and solubility parameter of asphaltene. It is worth noting that an accurate measurement of density and solubility parameters is more time-consuming than a measurement of the asphaltene molecular weight.[6−17] It has been reported that the thermodynamic models in the absence of extensive data fitting cannot well-predict asphaltene precipitation because of the lack of knowledge about asphaltene properties and some unjustifiable assumptions for molecular-weight estimation.[18−23]

The use of aggregation/gelation phenomena in the scaling model first presented by Rassamdana et al.[18,20] led to model independency on asphaltene properties. They claimed that asphaltene precipitation is similar to aggregation/gelation phenomena and thus used the scaling/fractal theory to describe asphaltene precipitation. The scaling model is a simple model that requires the dilution ratio, R, and molecular weight of injected fluid (called diluents), M_w, to predict the amount of asphaltene precipitation, wt %.[19−21] These variables were combined into two dimensionless variables X and Y, defined as follows:

$$X = \frac{R}{M_w{}^Z} \tag{1}$$

and

$$Y = \frac{\text{wt \%}}{R^{Z'}} \tag{2}$$

where Z' with a numerical value of -2 is recommended as a constant exponent that is independent of the type of crude oil and the precipitating agent and Z is considered as an adjustable parameter with the numerical value in the range of 0.25−0.6 depending upon the type of crude oil and precipitant.[20] The scaling equation has been represented in terms of X and Y by polynomial function

$$Y = A_1 + A_2X + A_3X^2 + A_4X^3 \tag{3}$$

The coefficients A_1-A_4 should be determined through data fitting using experimental data. The development of the scaling model by Rassamdana et al.[18,20] was based on data from Iranian southwest oil reservoirs. Later on, Hu et al.[24] applied a tuned scaling model to predict asphaltene precipitation for two kinds of heavy oils from Canada and the U.S. The effects of the temperature, molecular weight of *n*-alkane precipitants, and dilution ratio on asphaltene precipitation in a Chinese crude oil have been studied experimentally by Hu and Guo.[25] Hu et al. have also studied asphaltene precipitation because of CO_2 injection.[26] They proposed a generalized corresponding state principle (CSP) for the prediction of asphaltene precipitation. The CSP theory complemented the scaling equation for asphaltene precipitation under the influence of *n*-alkane precipitants. In their study, the parameters and exponents of a corresponding state equation was capable of describing the asphaltene precipitation behavior in the studied high-pressure CO_2-injected crude oil systems. They indicated that the generalized corresponding state theory was suitable for prediction of asphaltene precipitation from petroleum fluids as a result of the addition of miscible solvents at various temperatures and pressures. Thermodynamically, asphaltene precipitation is not independent of the reservoir pressure. However, the effect of the pressure is not included in the scaling model developed by Rassamdana et al.[18,20]

Menshad et al.[27] included the effect of the pressure on the nucleation onset and the amount of asphaltene precipitation in the scaling model. In the new scaling model, the relation between the dilution ratio and the molecular weight of diluents and the amount of asphaltene precipitation has been presented in two variables x and y as follows:

$$x = \frac{R}{M_w{}^Z} \tag{4}$$

and

$$y = \frac{\text{wt \%}}{R^{Z'}} \tag{5}$$

To include the effect of reservoir pressure on asphaltene precipitation in the new scaling model, the variables X and Y are defined as follows:

$$X = \frac{x}{P^{C_1}} \tag{6}$$

and

$$Y = \frac{y}{x^{C_2}} \tag{7}$$

In the new scaling equation, similar to the original scaling equation, Y has been expressed in terms of X by a polynomial function of eq 3. Thus, the new scaling equation includes seven adjustable parameters of A_1-A_4, C_1, C_2, and Z. These parameters should be estimated using experimental data. Scaling models to a less degree than thermodynamic models require parameter tuning to predict asphaltene precipitation for different oil and reservoir conditions assuming that necessary experimental data are available. Therefore, the need for parameter tuning for each specific oil and reservoir condition is the limitation of scaling models.

To remove such limitation, this study presents a comprehensive model to estimate asphaltene precipitation in a wide range of operation conditions and to determine the onset of

(20) Rassamdana, H.; Farhani, M.; Dabir, B.; Mozaffarian, M.; Sahimi, M. Asphalt flocculation and deposition. V. Phase behavior in miscible and immiscible injections. *Energy Fuels* **1999**, *13* (1), 176–187.

(21) Hirschberg, A.; DeJong, L. N. J.; Schipper, B. A.; Meijer, J. G. Influence of temperature and pressure on asphaltene flocculation. *SPE J.* **1984**, *24*, 283–293.

(22) Kokal, S. L.; Najman, J.; Sayegh, S. G.; George, A. E. Measurment and correlation of asphaltene precipitation from oils by gas injection. *J. Can. Pet. Technol.* **1992**, *31*, 24–30.

(23) Yang, Z.; Ma, C. F.; Lin, X. S.; Yang, J. T.; Guo, T. M. Experimental and modeling studies on the asphaltene precipitation in degassed and gas-injected reservoir oils. *Fluid Phase Equilib.* **1999**, *157* (1), 143–158.

(24) Hu, Y. F.; Chen, G. J.; Yang, J. T.; Guo, T. M. A study on the application of scaling equation for asphaltene precipitation. *Fluid Phase Equilib.* **2000**, *171*, 181–195.

(25) Hu, Y. F.; Guo, T. M. Effect of temperature and molecular weight of *n*-alkane precipitants on asphaltene precipitation. *Fluid Phase Equilib.* **2001**, *192*, 13–25.

(26) Hu, Y. F.; Li, S.; Liu, N.; Chu, Y. P.; Park, S. J.; Mansoori, G. A.; Guo, T. M. Measurement and corresponding states modeling of asphaltene precipitation in Jilin reservoir oils. *J. Pet. Sci. Eng.* **2004**, *41*, 169–182.

(27) Menshad, A. K.; Mofidi, A. M.; Shariatpanahi, F.; Edalat, M. Developing of scaling equation with function of pressure to determine onset of asphaltene precipitation. *J. Jpn. Pet. Inst.* **2008**, *51*, 102–106.

asphaltene precipitation. The presented model is based on an artificial intelligence (AI) method that is still in the primary stages of development and presents promising results that still require extensive study to be matured.[28] A Bayesian belief network (BBN) is applied particularly when the fundamentals of the model structure, cause−effect relation between variables, are faced with problems of conceptual uncertainty.[29−31] The preference of BBN among AI methods was due to the facts that (i) asphaltene precipitation is causative in nature, (ii) BBN is capable of extracting an interrelation between causes and effects quantitatively, and (iii) there is no limitation in the flow of information in a BBN model from causes to effects and vice versa. The later fact allows one to predict the dilution ratio at nucleation onset for a given pressure and diluent and trivial asphaltene weight percent. Moreover, the BBN model training using a complete databank covering oil conditions of interest removes the limitation associated with the scaling model. Because the required data for training does not include asphaltene properties, one does not face difficulties associated with thermodynamic models in applying a trained BBN model.

A very brief introduction to fundamentals of BBN is included as a background, and then the BBN model was developed to predict asphaltene precipitation. Required experimental data for training of the BBN model is not available in the literature. To generate such data, a high-pressure apparatus was designed and commissioned to carry out asphaltene precipitation tests and data collection. A comparison was also made between the BBN model predictions and the scaling model predictions.

2. BBN

A BBN is a graphical probabilistic model to represent and study an uncertain domain. A BBN can also be used to deal with the systems that are of a cause−effect nature. However, a BBN is a mathematical structure that uses conditional independences for the speed of inference, instead of a real model of causalities. Historically speaking, a suggested link between causality and conditional independence, indeed, goes back to Reichenbach.[32] Representing conditional independences, which can be obtained as consequences of the causal relationships, provides a natural and consistent way to express what is known about the different phenomena. Probabilistic relationships, such as conditional independencies, can be used to investigate the causal structure dealing with uncontrolled observations.[33]

To acquire a better understanding of the conditional independence, the following example can be considered. A driver is supposed to make a long trip. To analyze the risk of him falling asleep while driving, two cases can be considered. The first one is that he feels tired when he starts his trip, and the second one is that he is not tired at the beginning of the trip. It is evident that the amount and the quality of the driver's sleep, his fatigue, and the risk of him falling asleep have causal relationships. However, as in the first case, if it is known that he is tired, then the reason of his fatigue, whatever it is, can be considered of no use in evaluating the risk of him falling asleep. The same conclusion as drawn for the first case can be made for the second one, in which it is known that the driver does not feel tired at the beginning of the trip. Thus, it can be considered that the quality of his sleep before the trip has no influence on the risk of him falling asleep. Therefore, once it is known if the driver is tired, the quality of the driver's sleep does not provide additional information for evaluating the risk of him falling asleep. In statistical terminology, the risk of him falling asleep is said to be conditionally independent of the driver's quality of sleep given the driver's fatigue.[34] Mathematical definition and more examples of the conditional independence can be found elsewhere.[33,34]

A BBN consists of a set of nodes and directed edges between nodes. Nodes represent uncertain events or variables. Nodes can be in either a continuous or discrete random format. The states bin ranges of a discretized node are exclusive. Development of a BBN that comprises continuous and discretized nodes is possible.[35] The directed edges are the links between a pair of nodes, and their direction represent causal influence of one node (parent node) on the other one (child node). In the context of BBN, each node is associated with a probability distribution. Nodes without parents are called root nodes and have an associated prior probability (PP) distribution. For child nodes, the probability distribution takes the form of conditional probability (CP) that represents the correlation between a parent and a child node. The edges of a BBN represent the statement that each variable is conditionally independent of its non-descendents in the graph given its parent in the same graph.[36] The conditional independence assertions can augment the speed of inference. It should be noted that a connection between two nodes does not and need not always imply causality.[37] The connection essentially implies a direct influence of the parent node on the child node in the way that the probability of the child node is conditional on the probability of the parent node. A BBN requires four basic elements to represent our knowledge of the process under consideration: set of nodes, directed edges, conditional probability distribution, and prior probability distribution.

New information for a variable, called evidence, can be used to instantiate the node representing the variable by setting the probability of one of the states of that node to 100 (on a percentage basis). The number of nodes receiving evidence can be different from one to many at different times depending upon information availability. Introducing evidence to a model allows for the updating probability distribution of

(28) Sayyad Amin, J.; Escrochi, M.; Mehranbod, N.; Namazirad, M. H.; Ayatollahi, S.; Alamdari, A. Presented at the 10th International Wetability Conference, Abu Dhabi, United Arab Emirates, Oct, 2008.

(29) Mehranbod, N.; Sorush, M.; Piovoso, M.; Ogunnaike, B. A. Probabilistic model for sensor fault detection and identification. *AIChE J.* **2003**, 1787–1802.

(30) Mehranbod, N.; Sorush, M.; Panjapornpon, C. A method of sensor fault detection and identification. *J. Process Control* **2005**, *15*, 321–339.

(31) Lauritzen, S. L.; Spieglhalter, D. J. Local computations with probabilities on graphical structures and their application to expert systems (with discussion). *J. R. Stat. Soc., Ser. B* **1988**, *50*, 157–224.

(32) Floridi, L. *The Blackwell Guide to the Philosophy of Computing and Information*; Blackwell Publishing Ltd.: Oxford, U.K., 2004; ISBN: 0-631-22919-1.

(33) Pearl, J. *Causality—Models, Reasoning, and Inference*; Cambridge University Press: Cambridge, U.K., 2000; ISBN: 0-521-77362-8.

(34) Pourret, O. Introduction to Bayesian networks. In *Bayesian Networks: A Practical Guide to Applications*; Pourret, O., Naïm, P., Marcot, B., Eds.; John Wiley and Sons, Ltd.: Chichester, U.K., 2008; ISBN: 0-470-06030-1.

(35) Korb, K. B.; Nicholson, A. E. *Bayesian Artificial Intelligence*; Chapman and Hall/CRC: London, U.K., 2004; ISBN: 1-584-88387-1.

(36) Langseth, H. Bayesian networks in reliability: The good, the bad, and the ugly. In *Advances in Mathematical Modeling for Reliability*; Bedford, T., Quigley, J., Walls, L., Alkali, B., Daneshkhah, A., Hardman, G., Eds.; IOS Press: Amsterdam, The Netherlands, 2008; ISBN: 1-586-03865-6.

(37) Alpaydin, E. *Introduction to Machine Learning*; MIT Press: Cambridge, MA, 2004; ISBN: 0-262-01243-X.

uninstantiated nodes that can be used to calculate numerical values for such nodes as predictions. The mathematical procedure to update probability distribution is called "inference", and Bayes' rule is the basis for carrying out the inferences in a BBN. When there is a shortage of information, the evidence of the probabilistic BBN model help us update our knowledge of the process, even in the case of inaccurate data. This is an advantage of BBN over other modeling methods that do not deliver any result when a set of inputs is not complete.

The learning capability of the BBN is one of its prominent features[38,39] because it helps one to discover the correlation between different system information. Learning allows for either developing the structure of a BBN model, qualitative learning, or updating an existing BBN model to fit new system information, quantitative learning. In the former system, information is used to determine the cause−effect relation between nodes or directed links. However, in the later system, information is applied to update an existing BBN model by changing CP data.

3. Development of the BBN Model

The model presented in this study is founded on the basis of the scaling/fractal theory; therefore, the same variables used in the scaling/fractal theory are employed here. In this model, the dilution ratio, pressure, and molecular weight play the role of parent nodes and the asphaltene weight percent plays the role of the child node. The links between nodes are based on the scaling model, which is shown in Figure 1. All nodes in the model of Figure 1 are of discrete format. The selected state bin ranges are based on our knowledge of asphaltene precipitation and other variables. The maximum amount of asphaltene precipitation exists in the ranges between 0 and 2100 psia. In some research, this amount was considered to happen at 5500 psia, with an observed constant weight percent from 2100 to 5100 psia.[18−20] Six states have been assigned for the pressure node. The first five that cover 0−5100 are equally spaced. State bin ranges for the dilution ratio and asphaltene precipitation node were unequal. These different bin range assignments are made on the basis of the experimental data obtained using the high-pressure apparatus and various research papers.[13,18−24] Diluents include *n*-alkanes that can affect asphaltene precipitation in crude oil. The most common diluents are *n*-pentane, C_5, *n*-hexane, C_6, and *n*-heptane, C_7. In the BBN model, the molecular weight of these three *n*-alkanes were considered as states of the node representing diluents. The node, state names, and bin ranges/values in the BBN model of Figure 1 are represented in Table 1. The state prior probability distributions of all nodes are considered to be uniform.

To this end, among four basic elements of a BBN, the first three are determined and the last one is the only requirement to complete a BBN model. This can be determined via a quantitative learning process using experimental data on asphaltene precipitation under different conditions. Because of the lack of experimental data in relevant literature,[18−24] an apparatus was designed and operated to prepare an as rich as possible data set for BBN model training.

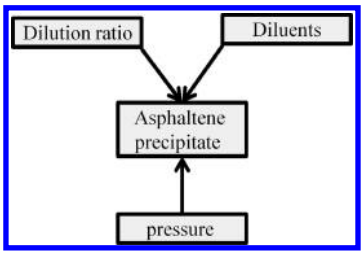

Figure 1. Structure of the developed BBN for asphaltene precipitation.

4. Training and Testing of BBN Models

After the BBN model development, its training should be performed. To investigate the performance of the BBN model, available data should be divided into two separate data sets. One data set is used for the training of the BBN model, and the other one is employed for its testing. To investigate the sensitivity of the model with respect to the sampling, assigning the available data to each set is randomly performed. The process can be repeated several times to explore the performance of the BBN model.

In the current study, Netica software (Norsys Software Corp., Vancouver, British Columbia, Canada)[40] was used as an interface to construct the structure of the BBN model, train the model, and perform the inference. To learn from data, Netica can use three learning algorithms: counting, expectation−maximization (EM), and gradient descent.[40] The first algorithm is the fastest and simplest one, but it is not suitable whenever missing data or uncertain findings in some nodes exist. Among the three, EM is the most robust one (i.e., it gives good results in a wide range of circumstances). Most experimental databases contain missing data. This is also the case for investigating pressure effects on the asphaltene precipitation. Although, in the current research, a special apparatus has been designed to obtain more data points, there are some regions of the pressure in which few data points are available. As previously mentioned, in such cases, the EM algorithm is one of the best and most robust quantitative learning algorithms to apply when missing data are present. Therefore, in this study, the EM[41] learning algorithm was selected to generate required conditional probability data. In short, the EM learning algorithm repetitively updates conditional probability data of a Bayes net to arrive at a better one by performing an expectation (E) step pursued by a maximization (M) step. In the E step, it uses regular Bayes net inference with the existing Bayes net to compute the expected value of all unobserved data, and then the M step acquires the maximum likelihood of Bayes net given the extended data (i.e., original data plus expected value of the unobserved data). Detailed discussions on BBN learning algorithms can be found elsewhere.[42,43]

Improvement of the current algorithms for learning from incomplete or sparse data sets is one of the ongoing research issues in the field of computer science,[44] and application of the

(38) Jensen, F. V. *An Introduction to Bayesian Networks*; Springer-Verlag: New York, 1996; ISBN: 0-387-91502-8.
(39) Pearl, J. *Probabilistic Reasoning in Intelligent Systems: Networks of Plausible Inference*; Morgan Kaufmann, Inc.: San Francisco, CA, 1988; ISBN: 1-558-60479-0.
(40) Norsys. *Netica Application for Belief Networks and Influence Diagrams: User's Guide*, versions 1.05 for Windows; Norsys Software Corporation: Vancouver, British Columbia, Canada, 1996.
(41) Dempster, A. P.; Laird, N. M.; Rubin, D. B. Maximum likelihood from incomplete data via the EM algorithm. *J. R. Stat. Soc.* **1977**, *39* (1), 1–38.
(42) Russell, S.; Norvig, P. *Artificial Intelligence: A Modern Approach*; Prentice Hall: Englewood Cliffs, NJ, 1995; ISBN: 0-136-04259-7.
(43) Neapolitan, R. E. *Learning Bayesian Networks*; Pearson Prentice Hall: Upper Saddle River, NJ, 2004: ISBN: 0-130-12534-2.
(44) Liao, W.; Ji, Q. Learning Bayesian network parameters under incomplete data with domain knowledge. *Patten Recognit.* **2009**, *42* (11), 3046–3056.

Table 1. State Names and Bin Ranges/Values in the BBN Model of Figure 1

variable	state name	states bin ranges/values		
diluents	C_5-C_7	C_5 = *n*-pentane (M_w = 720) C_6 = *n*-hexane (M_w = 86.116) C_7 = *n*-heptane (M_w = 100.21)		
dilution ratio	r_0-r_9	$0 < r_0 < 1$	$0.1 \le r_1 < 2$	$2 \le r_2 < 3$
		$3 \le r_3 < 5$	$5 \le r_4 < 8$	$8 \le r_5 < 10$
		$10 \le r_6 < 12$	$12 \le r_7 < 15$	$15 \le r_8 < 17$
			$17 \le r_9 < 20$	
pressure (psi)[a]	p_0-p_5	$0 < p_0 < 100$	$100 \le p_1 < 1100$	$1100 \le p_2 < 2100$
		$2100 \le p_3 < 3100$	$3100 \le p_4 < 4100$	$4100 \le p_5 < 5100$
wt % asphaltene precipitation	w_0-w_{10}	$0 < w_0 < 0.15$	$0.15 \le w_1 < 0.5$	$0.5 \le w_2 < 1$
		$1 \le w_3 < 1.5$	$1.5 \le w_4 < 2$	$2 \le w_5 < 2.5$
		$2.5 \le w_6 < 3$	$3 \le w_7 < 3.5$	$3.5 \le w_8 < 4$
		$4 \le w_9 < 4.5$	$4.5 \le w_{10} < 5$	

[a] 1 psia = 6.895×10^3 Pa.

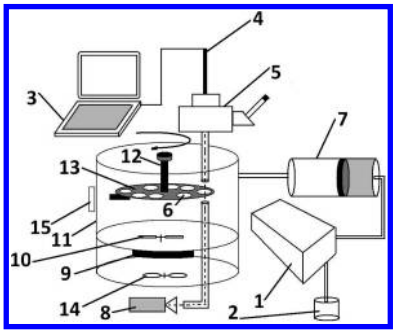

Figure 2. Schematic diagram of the experimental apparatus including (1) peristaltic pump, (2) distilled water reservoir, (3) computer, (4) CCD camera, (5) microscope, (6) sight glass, (7) piston cylinder, (8) cold light source, (9) heater, (10) magnetic mixer, (11) high-pressure cell, (12) rotator, (13) metal disk, (14) fan, and (15) magnetic device.

newly developed algorithms can be pursued for future studies in chemical and petroleum engineering.

5. Apparatus and Procedure

The evolution of asphaltene precipitation was monitored by an image processing method. A detailed description of the experimental apparatus is reported elsewhere.[45] The schematic diagram of the apparatus used in this study is illustrated in Figure 2. The main part of the apparatus consists of a high-pressure cell, which is filled with crude oil. A rotating metal disk is placed horizontally inside the cell. Substrate plates of different types can be mounted on the disk to study the evolution of asphaltene precipitation.

Eight transparent substrates were placed on the holes of the rotating metal disk. The substrates were expected to collect asphaltene precipitation during experimental tests. The microscope with an optical resolution up to 480× was installed on the top of the cell to capture the high-resolution images of asphaltene precipitates on the substrates. Glass substrates were 0.5 × 0.5 mm. The movement of the rotating disk was controlled through a magnetic device from outside of the cell to keep each substrate in front of the microscope for a certain time. A source of cold light installed inside the cell was supplied to lighten the dark solution without the generation of excess heat. Crude oil is placed on the substrate in the gap between the microscope and light source. Clear images of particles in space between the substrate and microscope may be precisely captured by the microscope. To capture the microscopic images, a charge couple device (CCD) camera with a resolution up to 5.7 megapixels is installed just above the microscope. The resolution of the images is controlled by the operator and is stored in the computer for further analysis. This device is also able to capture video films during the precipitation process. Geometrical properties of asphaltene aggregation are determined by analyzing the captured images by Sigma Scan Pro 5 software. The pressure of the cell was maintained using a high-pressure liquid chromatography (HPLC) pump. The maximum pressure of 2100 psi can be maintained in this cell. The temperature of the cell could be adjusted using a heater installed outside of the cell.

Table 2. SARA Analysis of the Crude Oil[44]

number	test name	test method	result (wt %)
1	total acid number	ASTM D 664	3.94
2	saturate content	SARA test	48.02
3	aromatic content	SARA test	34.15
4	asphaltene content	SARA test	5.3
5	resin content	SARA test	8.5

Crude oil with an API of 29.42° used in this study was supplied from a reservoir located in southwest of Iran. The saturate, aromatic, resin, and asphaltene (SARA) analysis of the crude oil used is listed in Table 2.

Different *n*-alkanes (*n*-pentane, *n*-hexane, and *n*-heptane) of HPLC grade from Merck Company were used as the precipitating agents.

To investigate the asphaltene precipitation, a series of experiments were carried out through the following procedure: (1) 150 cm^3 of crude oil was poured into the cell, and the system temperature was fixed to 70 °C. (2) A certain amount of solvent at a specific dilution ratio was added and mixed slowly using a magnetic mixer. (3) The system pressure was increased gradually until the precipitation started (onset pressure) and then continued to 2100 psia. This measurement requires skill and repetition. (4) The precipitated asphaltene particle on the substrate surface was monitored during the evolution of the precipitation process. The images of asphaltene aggregates with various sizes and shapes were clearly visible *in situ*. (5) The geometric properties and size distribution of asphaltene aggregates from images were calculated by image analyses. The volume and mass of asphaltene precipitates on the substrate at different pressures and dilution ratios were calculated through size distribution. (6) The experiment was repeated at different conditions with new samples of crude oil.

Three images were used to determine the average size distribution of asphaltene particles for each case. The number of precipitated particles in each image was in the range of 1100−1800. The mass of asphaltene precipitated was calculated using the average size distribution and density.

6. Results and Discussion

6.1. Predictions Based on the BBN Model. As mentioned previously, quantitative learning of the BBN model of

(45) Sayyad Amin, J.; Ayatollahi, S.; Alamadari, A. Fractal characteristics of an asphaltene deposited heterogeneous surface. *Appl. Surf. Sci.* **2009**, *256*, 67–75.

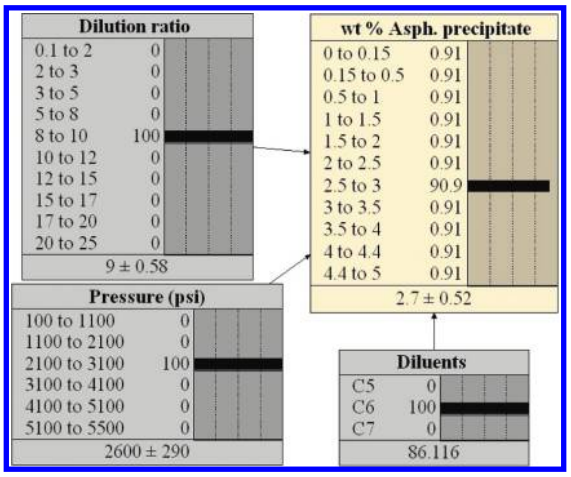

Figure 3. Sample of the performing inference process in the developed BBN.

Table 3. Relative Absolute Deviation Errors for the 10 Test Data Sets

test data set number	$\sigma \times 100$
1	4.56
2	4.45
3	4.6
4	4.7
5	4.1
6	4.6
7	4.8
8	4.4
9	4.4
10	4.4
average	4.501

Figure 1 to determine CP data requires experimental data that was mainly obtained using the experimental setup. To enrich the databank used for BBN model training, 20 experimental data points from the literature[18−20] were added to the data points obtained in this study. The significance of these 20 data points was due to the fact that they were obtained in the pressures above 2100 psia and that the oil used in the present study was similar to the one used in the published research.[18−20] Around 80% of data points (560 data points) were randomly selected to train the BBN model. The rest of the data points (20%) was used for testing model predictions.

The available data were divided into two data sets for training and testing of the model. To investigate the validity and performance of the BBN model and also to explore its sensitivity with respect to the sampling, the selection of test and training data sets was randomly performed 10 times. For each model, the relative absolute deviation error (σ) was calculated as follows:

$$\sigma = \sum_{i=1}^{n} |(Y_i^{\exp} - Y_i^{\text{model}})/Y_i^{\exp}| \qquad (8)$$

where $Y^{\exp}$ and Y^{model} stand for the experimentally measured asphaltene precipitation percents and those obtained from the BBN model (for different test data sets), respectively. The obtained errors are reported in Table 3. The average of the relative absolute errors is relatively small (4.5%), which indicates the validity and suitable performance of the model. On the other hand, the obtained errors for different test data sets were more or less the same. It can be revealed that the model is not sensitive to the sampling issue.

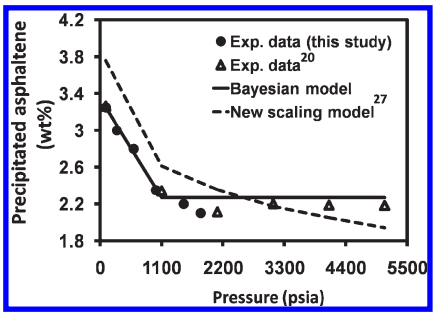

Figure 4. Comparison of the BBN and scaling equation for the prediction of asphaltene precipitation (wt %) at different pressures (*n*-hexane as the precipitant; $R = 3$ cm^3 of solvent/g of oil).

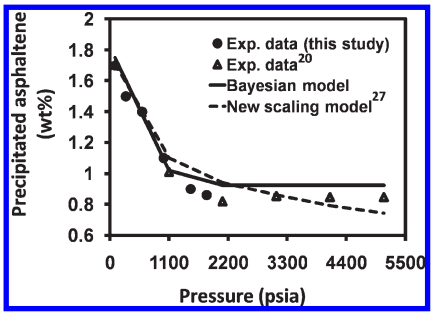

Figure 5. Comparison of the BBN and scaling equation for the prediction of asphaltene precipitation (wt %) at different pressures (*n*-heptane as the precipitant; $R = 3$ cm^3 of solvent/g of oil).

Figure 3 depicts a sample of the network developed in Netica including nodes, directed links, and state bin ranges for the case having the least relative absolute error.

The probability distributions shown in this figure correspond to a case in which evidence has entered the network through the pressure, molecular weight, and diluents by instantiating the probability distribution of these nodes. As expected by instantiating, 100% probability is assigned to only one state in these nodes and the probabilities of the other states are assigned as 0%. The inference process updates the prior probability of the node wt %. An asphaltene precipitate as shown in Figure 3, and the numerical value assigned by the inference process to this node is calculated as 2.7 ± 0.52.

To test capabilities of the BBN model, the predictions by the model have been compared to those obtained using the new scaling model[27] and experimental data of other studies.[20] Considering the importance of the pressure effect on the asphaltene precipitation in the reservoirs, the variation of the asphaltene weight percent with pressure was obtained from the BBN model. To obtain asphaltene weight percents, the pressure was changed, while the other two inputs of the model were kept constant. The same procedure was repeated for different diluents (*n*-hexane and *n*-heptane) and for a constant dilution ratio, which was 3 cm^3 of diluents/g of oil. Although the graphs are depicted for a constant dilution ratio, needless to say, the model was capable of considering the effect of different dilution ratios on the asphaltene precipitation. The comparisons for *n*-hexane and *n*-heptane are shown in Figures 4 and 5. These figures suggest a better agreement between the experimental data and the BBN model predictions compared to the predictions of the new scaling model. It is notable that only 16 data points above 2100 psia were used to train the BBN model. It should be

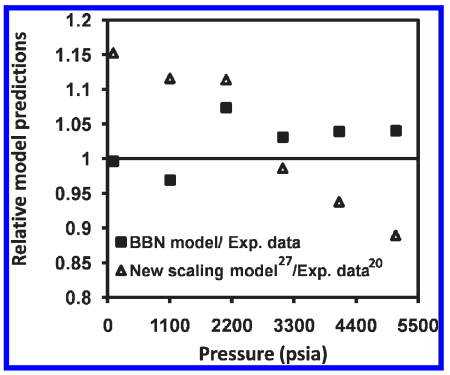

Figure 6. Accuracy of the BBN model compared to the scaling model at different pressures (*n*-hexane as the precipitant; R = 3 cm^3 of solvent/g of oil).

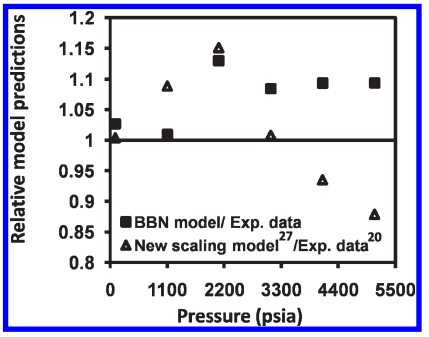

Figure 7. Accuracy of the BBN model compared to the scaling model at different pressures (*n*-heptane as the precipitant; R = 3 cm^3 of solvent/g of oil).

Table 4. Values of Standard Deviation and Coefficient of Determination for the New Scaling Method and BBN Model

model	diluent	R^2	standard deviation
BBN	*n*-hexane	0.9642	0.4042
new scaling model		0.5544	0.6732
BBN	*n*-heptane	0.9660	0.3212
new scaling model		0.9493	0.5895

noted that, although the structure of the BBN model including the bin size assignments may not be optimal, the simulation results of the BBN model are comparable to those of the scaling model and have good agreement with the experimental values. Further studies are required to explore the effect of different bin size assignments on simulation results and to determine optimum bin size assignments.

Figures 6 and 7 demonstrate the comparison between predictions of the BBN model and scaling model on a dimensionless basis, in which predicted values are divided by experimental values. The standard deviations and the coefficients of determination (R^2) were calculated and reported in Table 4. The high value of the coefficient of determination indicates the appropriate performance of the BBN model.

The average relative deviations of the BBN model and new scaling model predictions are less than 4.5 and 12%, respectively. The higher average relative absolute deviations in predictions of the BBN model at pressures over 2100 psia that is 7.69% compared to 3.32% at lower pressures can be attributed to the fact that only 16 data points in this range were used for network training.

The capability of the BBN in the prediction of asphaltene precipitation at different dilution ratios for different diluents

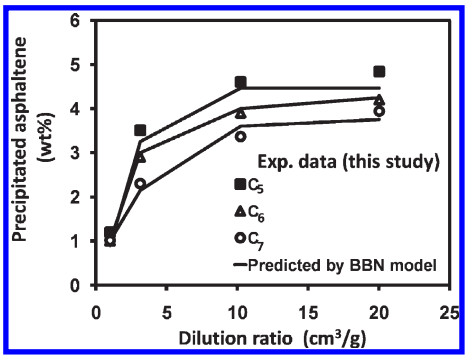

Figure 8. Comparison of the prediction of asphaltene precipitation (wt %) by the BBN model with experimental data for various dilution ratios and *n*-alkanes at atmospheric pressure.

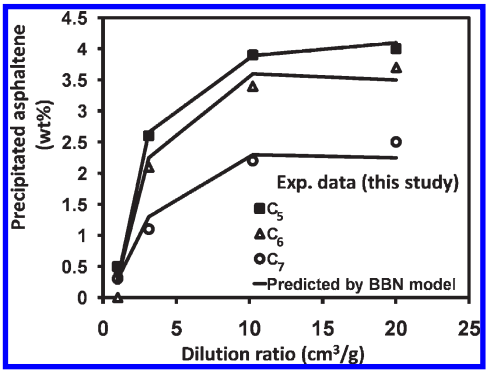

Figure 9. Comparison of the prediction of asphaltene precipitation (wt %) by the BBN model with experimental data for various dilution ratios and *n*-alkanes at high pressure (2000 psia).

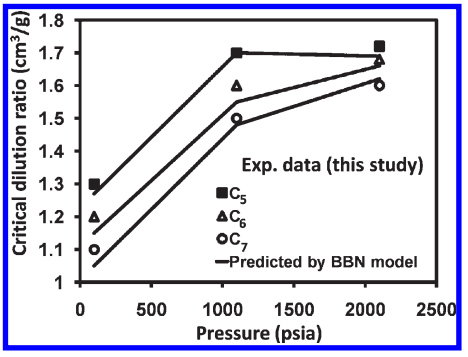

Figure 10. Comparison of the prediction of critical dilution ratio by the BBN model with experimental data for various *n*-alkanes at different pressures.

is shown in Figures 8 and 9. The BBN predictions are generally in good agreement with the experimental data.

6.2. Prediction of the Onset of Asphaltene Precipitation. The prediction of the asphaltene precipitation onset point is of practical importance. In addition to proposing a model for the prediction of asphaltene precipitation, the capability of the model for the prediction of the onset is another important feature of the model. The critical dilution ratio R_C is defined as the dilution ratio at the onset of asphaltene precipitation. The critical dilution ratio for different conditions can be obtained from the BBN model of Figure 1 directly without any additional structural change and training. In this study, the onset point was determined at different conditions using images from the high-resolution microscope. The predictions of the critical dilution ratio by the BBN model for test

data have been shown in Figure 10. It can be seen that the predicted critical dilution ratio for various *n*-alkanes at different pressures agree well with the experimental data measured.

7. Conclusions

An experimental setup was designed and commissioned for measuring the amount of asphaltene precipitation. The amount of asphaltene precipitation of a southwest Iranian oil reservoir was measured at different pressures and at a fixed temperature. Different normal alkenes (pentane, hexane, and heptane) were used as precipitation agents. A BBN model based on the scaling/fractal theory was developed to predict the amount and onset of asphaltene precipitation. Few experimental data from the literature with those obtained in this study were used to train the BBN model. The results revealed that the BBN model predictions for asphaltene precipitation were more accurate than the new scaling model. Unlike the scaling model, the BBN model does not require new training for experimental data from different conditions. Once the BBN model was trained using a rich experimental data set, it was used to predict not only asphaltene precipitation but also the critical dilution ratio without any additional effort.

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Nomenclature

A = coefficient of eq 3
BBN = Bayesian belief network
C = parameter of eqs 6 and 7
CCD = charge couple device
CP = conditional probability
CSP = corresponding state principle
EM = expectation−maximization
M_w = precipitant molecular weight (g/mol)
P = pressure (Pa)
R = dilution ratio (cm^3 of diluents/g of oil)
R_C = critical dilution ratio (cm^3 of solvent/g of oil)
wt % = weight percent of asphaltene
x = variable defined by eq 4
y = variable defined by eq 5
X = variable defined by eqs 1 and 6
Y = variable defined by eqs 2 and 7
Z = adjustable parameter
Z' = universal exponent
σ = relative absolute deviation error