

Modeling in-situ upgrading of heavy oils by subsurface pyrolysis

A. PEREZ-PEREZ⁽¹⁾, M. MUJICA⁽¹⁾, I. BOGDANOV⁽¹⁾, B. CORRE⁽²⁾

(1) Open and Experimental Centre for Heavy Oil (CHLOE) affiliated to the University of Pau, France.

(2) CSTJF, Total, Pau, France.

This paper has been selected for presentation and/or publication in the proceedings for the 2014 Heavy Oil Congress. The authors of this material have been cleared by all interested companies/employers/clients to authorize dmg:events (Canada) inc., the congress producer, to make this material available to the attendees of WHOC14 and other relevant industry personnel.

ABSTRACT

An alternative method to steam injection for heavy oil recovery is the in situ upgrading (IU) process. The IU process implies to heat the oil sand in the reservoir to temperatures larger than 320°C for enough time to promote a series of cracking reactions. These reactions produce lighter oils and gases while a solid residue (pyrobitumen) remains underground.

In this paper, we describe a numerical formulation of the IU process. Our model couples a reactive model with a thermodynamic model. This is able to represent the phase distribution of some pseudo-components and decomposition reactions of heavy oil fractions. Reaction rates depend on temperature and concentration. Phase distribution was represented by K-values functions. The thermo-kinetic model plus a flow formulation was implemented in a commercial reservoir simulator (STARS from CMG).

In this work, the IU model was validated by comparison with experimental results for an IU experiment reported in the literature. Simulations show that results for oil productions per pseudo-components, oil sample quality and mass of solid residue from simulation model are in good agreement with experimental measurements.

INTRODUCTION

The total bitumen reserves are estimated at 250 billion barrels globally, of which 180 billion barrels are in Canada. Bitumen is defined as oil that has an oil viscosity greater than 10k cP under reservoir conditions and API gravity less than 10 degree API. Due to its large viscosity, thermal methods are generally employed to produce it. One of the most popular thermal methods is the Steam Assisted Gravity Drainage process (SAGD) (Butler & Stephens, 1981). An alternative method to steam injection for heavy oil recovery is the in situ upgrading (IU) process (Kumar *et al.*, 2011). The IU process implies to heat the oil sand in the reservoir to temperatures larger than 320°C for enough time to promote a series of cracking reactions. These reactions produce lighter oils and gases while a solid residue (pyrobitumen) remains underground. The IU process is also a promising technology for oil shale reservoir.

Recently, some laboratory experiments were carried out on a reservoir unconsolidated core (Kumar *et al.*, 2011). Our goal in this paper is to reproduce the experimental results obtained in this experiment. To accomplish this, we developed an in-house code for coupling the reactive model with the thermodynamic model. This was able to represent the decomposition reactions of heavy oil fractions and the

of component X_i . The reactant mass-stoichiometric coefficient, d_i^j , is equal to one for this system.

In addition, mass conservation is applied to weight fractions per kinetic class

$$\sum_{j=1}^{N_r} w_{i,j} = 1 \quad (2)$$

and also for each reaction j in the product side (right),

$$\sum_{j=1}^{N_r} \sum_{i=1}^{N_c} d_i^j = 1 \quad (3)$$

Kinetics (activation energies and pre-exponential factors) and stoichiometric parameters ($w_{i,j}$ and d_i^j) were numerically calibrated according to pyrolysis mass balances. Reactions for each class are supposed to have the same frequency factor. Results were obtained from an optimization procedure. This is in essence a simple mass balance between reactive and products. The net balance between reactive and product must be zero.

If we define $\alpha_i^{j,\beta}$ as the pseudo stoichiometric coefficients of the component i (in molar basis) for the reaction j in phase β :

$$\alpha_i^{j,\beta} = \frac{d_i^{j,\beta} \cdot M_{w,s_j}}{M_{w,i}} \quad (4)$$

- The mass-stoichiometric coefficient for component i in the reaction j in phase β , $d_i^{j,\beta}$
- the molecular weight of the reactive component s_j in reaction j , M_{w,s_j}
- the molecular weight (mass per number of moles) for component i , $M_{w,i}$

The expression that control the reaction rate in molar basis for a first order reaction rate is

$$\frac{d}{dt}(N_i) = -\phi V \sum_{\beta=1}^{N_p} S_{\beta} \sum_{j=1}^{N_r} \alpha_i^{j,\beta} k_j^{\beta} n_j^{\beta} \quad (5)$$

- the total fluid volume $\phi V = \sum_{\beta=1}^{N_p} V_{\beta}$
- the saturation $S_{\beta} = \frac{V_{\beta}}{(\phi V)}$ of each phase
- the number of moles N_i in all phases
- the molar density n_i^{β} of component i in phase β

- the constant rate k_j^{β} for reaction j in phase β

The negative sign implies that a reactant is consuming. The reaction rates were directly proportional to the rate constant, K_i . The constant rate follows Arrhenius temperature dependence composed by a pre-exponential factor A_i and activation energy, E_{ai} .

$$K_i = A_i \exp - (E_{ai}/RT) \quad (6)$$

The set of ordinary differential equations for the pyrolytic model was decomposed into a set of elementary reactions (pathway) for which the information is encoded in three matrices, related to the stoichiometric, rate constants and mass fraction term powered to an exponent of one (first-order reaction). This information was used to build and solve the ODE system. The pathway was decomposed into unidirectional elementary reactions. Then, mass conservation expressions for each component were written to each elementary reaction to obtain ODE system.

MODELING IU EXPERIMENTS IN GOLD CELLS

A 2-D radial model (5x5 mm, 1x360°, 8x18.75 mm) in a close system and the detailed first-order Arrhenius-type reaction model from Kumar et al. (2011) were used to reproduce the decomposition rate of pseudo-components in the gold cells experiments. At the initial state the gold cells were fulfilled of bitumen so there was neither sand nor water in the system. The main objective was to compare results from the kinetic model introduced in the reservoir model and reported results from the experiments.

Three temperatures were evaluated: 325, 350 and 370°C. The approach that two-reactive phases (oil and gas phase) where pseudo reactive components follow the same reaction rate in both phases was evaluated to catch the kinetic measurements performed in global mass basis. This approach honor the global kinetic model reported by the lab.

Figure 1 shows the resulted mass decomposition/generation of some pseudo-components at 350°C from the lab experiments and from the reservoir model. In general, the kinetic model built in the reservoir model was able to mimic the kinetic experiments.

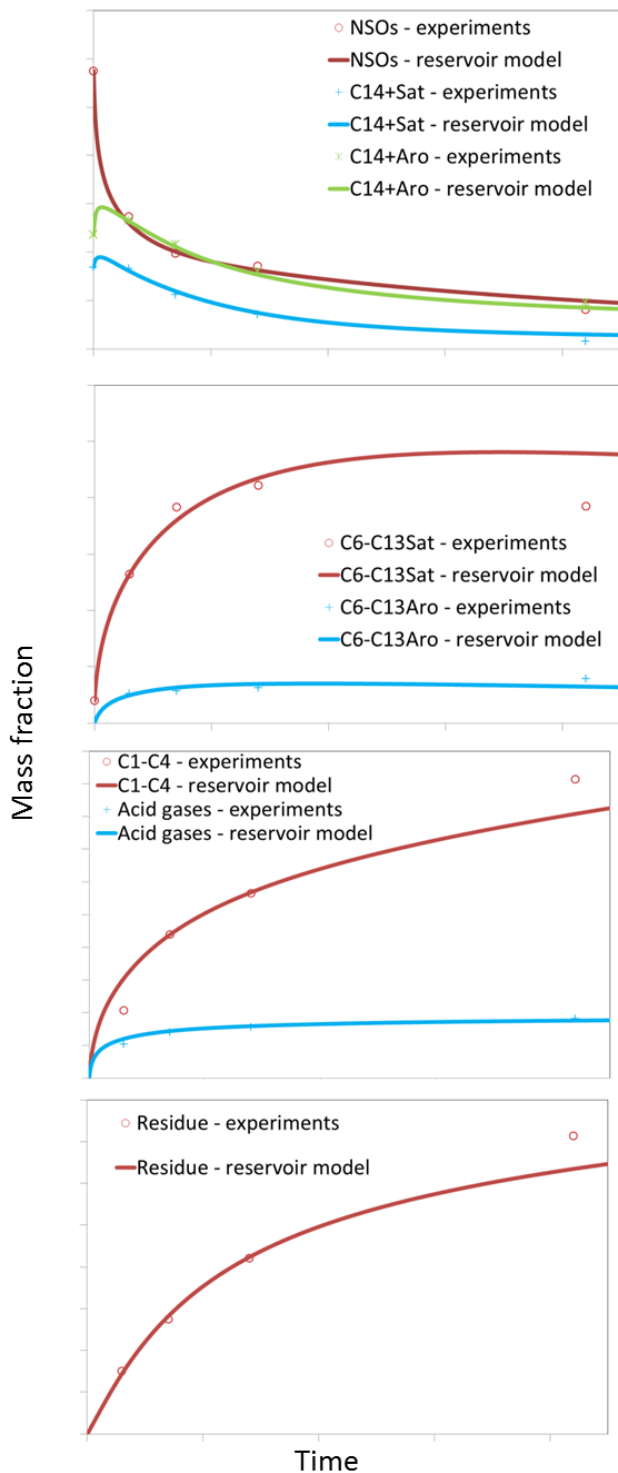


Figure 1: Pseudo-components mass evolution for the experimental model at 350°C as a function of time. Experimental value (dots), reservoir model in STARS (lines).

THERMODYNAMIC MODEL

Thermodynamic classes were imposed by kinetic model, as discussed in previous section, giving a total of twelve classes in the fluid model (solids components are not considered in the fluid model). In order to properly estimate required parameters for STARS for each thermodynamic class, an equation of state (EoS) approach was selected. Cubic EoS has been widely used in the oil industry for oil, and one of the most popular is the Peng-Robinson (PR) EoS (Peng & Robinson, 1978; Saber & Shaw, 2009). Thermodynamic characterization using PR requires three parameters for each component: critical temperature (T_c), critical pressure (P_c) and acentric factor (ω).

Thermodynamic classes' properties (T_c , P_c , ω) were estimated by group contribution methods. Marrero and Gani (2001) developed a generalized model of group-contribution method (GCM) for estimation of pure component properties: critical temperature, critical pressure, normal boiling point, critical volume; standard enthalpy of formation, standard enthalpy of vaporization, standard Gibbs energy, normal melting point and standard enthalpy of fusion. Estimation is performed at three levels; first level uses contributions from simple groups that allow describing a wide variety of organic compounds, the second and third level involve poly-functional and structural groups. The method of Constantinou *et al.*, (1995) was developed for pure component acentric factor and liquid molar volume at 298K. The basis is the same than the Marrero and Gani (2001) method, but the estimation is made only at two levels.

For multi-component mixtures, the extension of PR equation involves a linear mixing rule that include the use of binary interaction parameters between pseudo-components.

Peng-Robinson equation of state was fitted to available PVT data. Heavy fractions (NSO's) properties and binary interaction coefficients were used as fitting parameters. Figure 2 illustrate bubble pressure PR predictions against experimental data.

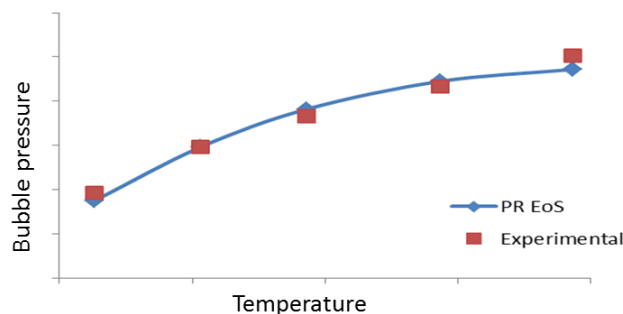


Figure 2. Bubble pressure fitting using PR equation of state.

Phase partition coefficients (K-values) for two-phase equilibrium are defined as the ratio between lighter phase molar composition (gas phase, y_i) and heavier one (liquid phase, x_i), as presented in the equation below. K-values (K_v) can be function of temperature (T), pressure (P) and molar composition of the mixture (z).

$$K_{v_i} = \frac{y_i}{x_i} = f(T, P, z) \quad (7)$$

In STARS, K-values can be expressed by tables or correlations. The table approach in STARS admits dependence in temperature, pressure and composition (defined only by one key-component). Temperature, pressure and key-component composition must be equal-spaced and cover the complete range of these variables. On the other hand, K-value correlations approach admits only dependence in temperature and pressure.

$$K_i = \left(\frac{K_{v1}}{P} + K_{v2}P + K_{v3} \right) \exp \left(\frac{K_{v4}}{T - K_{v5}} \right) \quad (8)$$

Proposed K-values estimation: In order to obtain estimation of K-values to be used in the simulation model of IUP experiments (open system), the solutions for a closed system were used. The kinetic model for a closed system was solved in Matlab (ODE solver) for a constant temperature to obtain the changes in composition over time. On the hypothesis of local thermodynamic equilibrium (Kristensen *et al.*, 2007), the Rachford-Rice equation was solved at each time increment (fixed T, P and z) in order to obtain K-values for the entire range of properties variation. A schematic representation of the proposed algorithm is presented in Figure 3. Using this procedure there were obtained a complete set of K-values for the whole temperature (10 - 400 °C), pressure (1 – 25 absolute bar) and composition range.

STARS constraints: once the temperature is above 250°C and chemical reactions begin in the in-situ upgrading process, the global composition starts to change as the reaction time increases. As it has been discussed previously, the IUP drastically changes the composition of the oil by converting heavy fractions into lights components (increase of API gravity) when the temperature reaches high temperatures ($T \geq 350^\circ\text{C}$). Analysis of the whole set of partition coefficients calculated revealed that these changes in oil composition occur at early-times and sharp changes in K-values are obtained, then after K-values are more or less constant. In STARS, the K-values tables should be smooth to avoid convergence problems. The use of composition dependent non-smoothed K-values was tested with unsuccessful results in the IU model. The proposed solution was to neglect short-

time changes and consider K-values not compositional dependence. K-value correlations were fitted for each pseudo-component (assuming $K_{v2}=K_{v3}=0$) and then used in the simulation model.

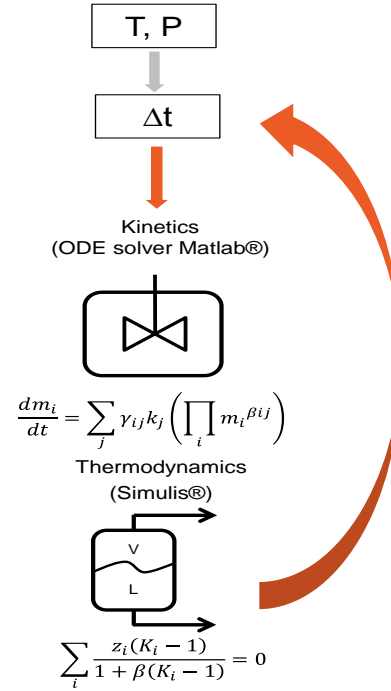


Figure 3. K-values calculation by pseudo-coupling between kinetics and thermodynamic models.

The viscosity for each pseudo-component (μ_i) was obtained from literature data for pure compounds and heavy ends were fitted to match dead oil viscosity. A linear logarithmic mixing rule function of molar composition (x_i) was assumed as presented in equation 9.

$$\ln(\mu) = \sum x_i * \ln(\mu_i) \quad (9)$$

Liquid molar densities (n) at each phase are obtained in STARS by applying a mixing rule with phase molar composition (x_i) as presented in Equation 10. Pseudo-components densities are modeled in STARS with an exponential law presented in equation 11 where liquid compressibility (CP), thermal expansion coefficients (CT1 and CT2) and pressure-temperature cross term for liquid density (CPT) are required parameters for each component.

$$\frac{1}{n_o} = \sum \frac{x_i}{n_{oi}} \quad (10)$$

$$n_{O_i} = n_{O_i}^{REF} * \exp \left[CP_i(P - P_{REF}) - CT1_i(T - T_{REF}) - \frac{CT2_i}{2}(T^2 - T_{REF}^2) + CPT_i(P - P_{REF})(T - T_{REF}) \right] \quad (11)$$

In equation 11, the term $n_{O_i}^{REF}$ refers to molar density at some reference conditions defined by the user, normally standard conditions at used (60°F and 1 atm).

Liquid mass density (ρ) for hydrocarbons is usually reported in terms of specific gravity (SG). At standard conditions (60°F and 1 atm) the density of liquid water (ρ_{water}) is 0.999 g/cm³.

Three sources of specific gravity (SG) estimations were considered in order to generate different scenarios of specific gravity estimations:

- Riazi (2005) presented SG at standard conditions values for some liquid hydrocarbons up to n-Docosane (C22H46).
- Riazi (2005) proposed a generalized SG correlation (equation 12) for different hydrocarbons families (n-alkanes, n-alkylcyclopentanes, n-alkylcyclohexane and n-alkylbenzenes). θ_∞ , θ , a and b are parameters tabulated for each hydrocarbon family.

$$SG = \frac{\theta_\infty - \exp(a - b * Mw^c)}{\theta} \quad (12)$$

- Simulis™ thermodynamic software (from ProSim) proposes internal correlations of density vs. temperature and pressure for pure compounds.

Different SG sources were evaluated for intermediate fractions (C2-C4; C5C13 and C14+). Values for heavier components (NSO's) were obtained by matching API gravity value of dead oil using a mass fraction (w_1) mixing rule.

IU EXPERIMENT

IU experiment was performed on unconsolidated cores of 0.05m diameter and 0.15 length. Porosity was around 0.30 while absolute permeability was 4158 mD. Initial water saturation and initial oil saturation were around 0.10 and 0.80 v/v at lab conditions, respectively and initial gas saturation was around 10% v/v. Table 1 summarizes experimental conditions and core properties.

The experimental procedure is described by Kumar et al., (2011). The core was mounted vertically in steel core holder divided in four equal zones for external heating. Internal and

external thermocouples were distributed in the core per section. The sections were heated progressively from the top to the bottom until the correspondent section reached the desired internal temperature. The heaters were programed to heat the core with a temperature gradient of 8°C/min. The producer well was placed on the cell top. The back pressure valve was fixed to operate at 15 bar in the producer well. The produced liquid was sampled at regular intervals and was analyzed for its composition using gas chromatography (GC) and gel permeation chromatography (GPC) process while gas phase composition was analyzed by GC. Tests were stopped until no more liquid fluids were produced. The duration of the experiment was 5.1 days. Five samples were taken during the IU experiment. Uncertainties in gas flow measurements were reported for this experiment.

Property	Value
Porosity, fraction	0.30
Permeability, mD	4158
Oil viscosity at 20°C, cP	319000
Molecular weight, g/gmole	487
Oil gravity, API	8.6
Initial pressure, bar	1
Initial temperature, °C	25
Initial oil saturation	0.77
Initial water saturation	0.11
Initial gas saturation	0.12

Table 1. Experimental conditions and core properties.

MODEL DESCRIPTION

A 2-D radial model was used to represent the IU experiment. Due to symmetry and the assumption of a homogeneous system, we model only half of the unit. Elemental grid-size was 0.005m length. Model size was 5 by 1 by 30. Only one slide in radial direction was considered (360°). Figure 4 shows a general description of the radial model.

Due to the presence of initial water saturation in the core, this component was also included in the model, giving a total of 30 pseudo-components in the simulation model. The components and phase distribution are shown in Table 2. The components having (*) means that two or more kinetic classes are represented in the same thermodynamic class. Methane, C2-C4 pseudo-component and CO2 and H2S were treated as non-condensable components. The non-soluble oils NSO1, NSO2 and NSO3 were only present in the oil phase.

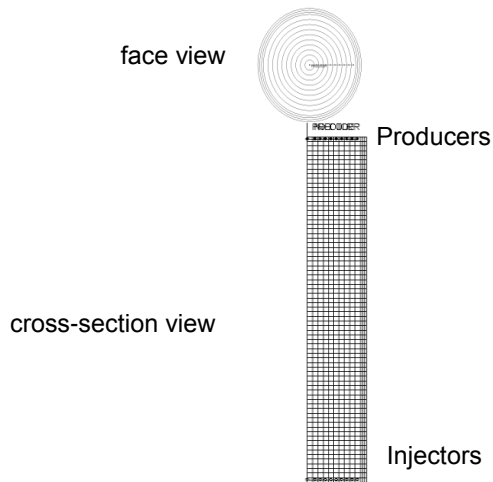


Figure 4. Simulation model.

Components/Phases	Aqueous	Oleic	Gaseous	Solid
Water	X		X	
C5-C13SAT (*)		X	X	
C5-C13ARO (*)		X	X	
C14+SAT (*)		X	X	
C14+ARO1 (*)		X	X	
C14+ARO2 (*)		X	X	
NSO1 (*)		X		
NSO2		X		
NSO3 (*)		X		
CO2			X	
H2S			X	
C1			X	
C2-C4			X	
Prechar				X
Residue				X

Table 2. Components and phase distribution for the IU model.

HISTORY MATCHING OF IU THE EXPERIMENT

For the IU experiment, the external temperature and the heat rate provide by the heaters were specified. The comparison between external calculated temperature profiles and measured temperature profiles is shown in Figure 5. Time series were cut from 0 to 1 day and temperature scale was cut from 300 to 400°C in order to appreciate difference between calculated and measured temperatures. Each series corresponds to different section from top to bottom. Top section has a 0.03 m length while the rest of sections have 0.04 m length. The external stationary temperature was 380°C until the end of the IU experiment (5.1 days).

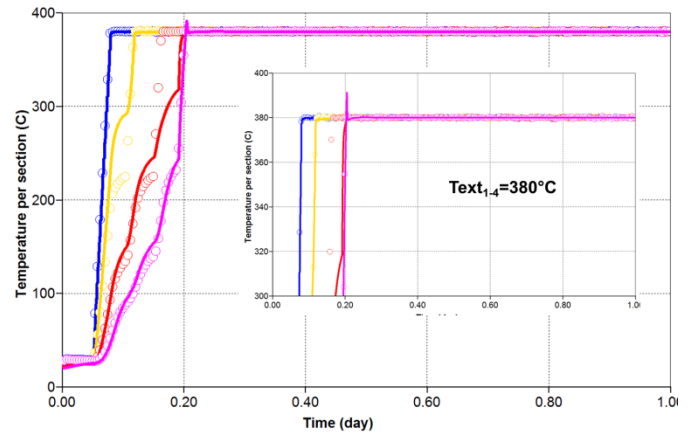


Figure 5. Experimental (dots) and calculated (lines) external temperatures for the four sections in the IU experiment.

The internal temperature was determined by the energy balance for the simulator. Internal temperatures obtained from the simulation and from the experiments are compared in Figure 5. Difference in temperature of 8°C and -6°C were reported for the experiment when compared internal and external temperature at stationary conditions. Differences in external and internal temperatures were not reproduced by the simulator at stationary conditions. Stationary internal temperature calculated by the simulator was constant and equal to 380°C. Reaction enthalpies are not described in the IU model due to lack of data. It believes that negative difference in internal and external temperatures are due to heat losses. This occurs in particular in those sections closer to the cell edges. It is not clear the reasons because internal temperatures are higher than external temperatures on the experiment when the IU process is mostly characterized by endothermic reactions.

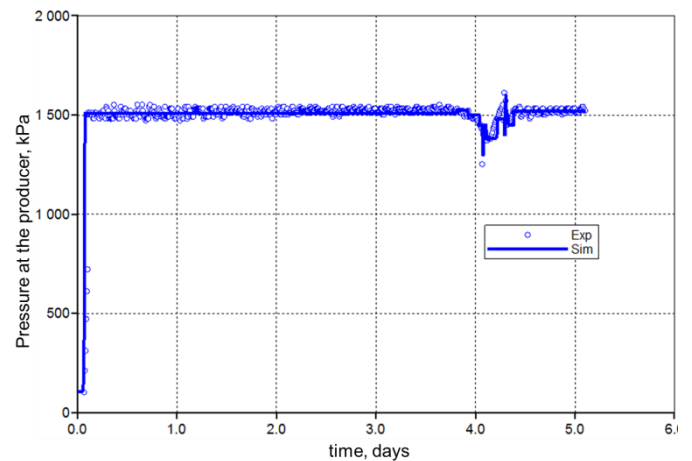


Figure 6. Pressure comparison at the cell top for the IU experiment.

Figure 6 compares pressure behavior on the cell top from the experiment and the simulation. Note that pressure increases with temperature at the beginning of the heating process from atmospheric condition to 1500 KPa (reference pressure for the back pressure valve).

A sensitivity analysis was performed to identify the effect of some parameters in the IU model based on experimental condition for the IU experiment. This analysis puts major emphasis on non-well known properties related to the core and physical properties for the C14+ fraction and non-soluble oil fraction (NSOs). The following features were analyzed:

- pressure variation during the inert gas injection
- stationary temperature
- initial gas saturation
- oil density model
- irreducible oil saturation
- Viscosity model
- Oil mobility
- Gas trapped in oil phase (foamy oil behavior)

The effects of these parameters in the IUP were analyzed during different experiment steps: thermal expansion process, IU process and gas flooding process. The following responses were analyzed:

- Oil production
- C5-C13 production
- C14+ production
- Solid mass distribution
- Distribution of prechar and residue at the end of the experiment
- API gravity in produced oil per collected samples

According to the sensitivity analysis results, properties like, density and thermal expansion coefficients, viscosity, relative permeability end-points seems to affect in some degree the IU process. Results obtained from this sensitivity analysis were useful in the history matching process.

Concerning to fluid production, a good match for oil and water production, oils pseudo-components production and API gravity were obtained for the IU experiment. Figure 7 show a comparative plot between oil and water production from the experiment and from the simulator. Three stages were identified for the IU process. The first stage controlled by the thermal expansion of fluids and water production (first to third sample points). A second step controlled by the IU process (from third to fifth sample points) and the third one, controlled by gas displacement (from fifth to sixth sample point). The in situ upgrading controlled step implies a smooth slope of hydrocarbon production (light to intermediate oil

fractions), most of them in gas phase at reservoir conditions according to simulation results. This step implies a slow oil production of improved hydrocarbons.

Figures 8 and 9 show comparative results between IU experiment and simulation results. Oil produced during the experiment was separated in C5-C13 fraction and C14+ fraction. Important differences are noticed during the thermal expansion process in the simulation which produces large oil fractions. This difference can be due to density model and the thermal expansion coefficients. During the IU process, the C5-C13 production is smooth. Most of light fractions are produced in gas phase at 1500 kPa and 380°C. Heavy fractions are not produced in important amount. Most of heavy fractions are produced during the gas injection process when a high injection rate of inert gas is injected for a short time period to sweep the core of whole fluids.

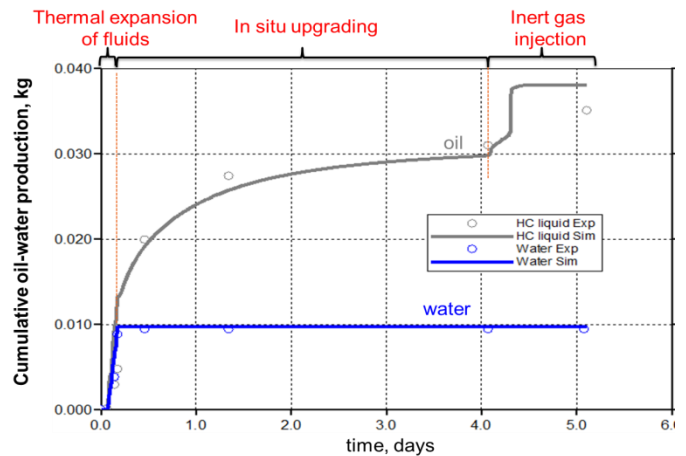


Figure 7. Cumulative oil and water production for IU experiment.

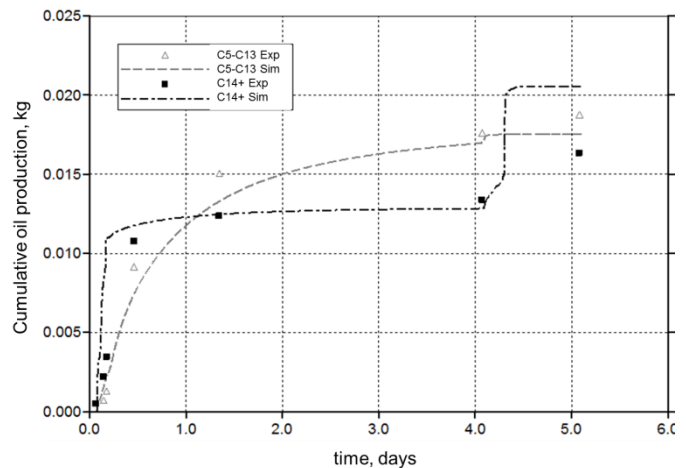


Figure 8. Cumulative C5-C13 and C14+ oil production for IU experiment.

Figure 9 shows the total solid generation (prechar + residue) estimated by the simulation as a function of time in the whole core and the value reported for the IU experiment. Experimental value is sensibly higher. It is worth noting that the estimated pyrobitumen generation in a close system (no production) at 5.1 day was 0.022 Kg. Difference in the total amount of pyrobitumen suggests that a different kinetic could have followed during the IU experiment.

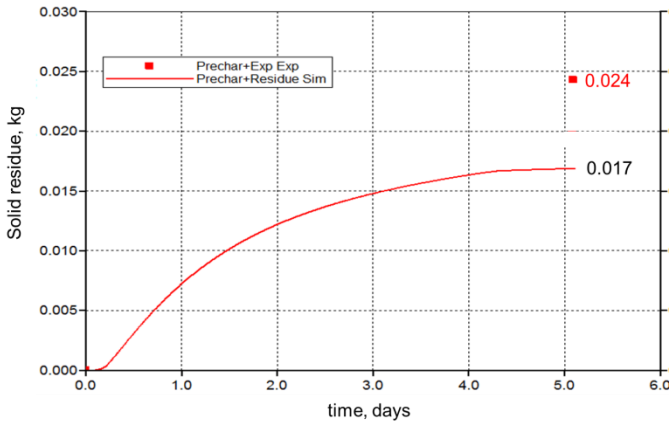


Figure 9. Solid generation in the core for the IU experiment.

Figure 10 shows the solid mass distribution in weight percentage along the core at the end of the IU experiment. Top section was 0.03 m length while the rest of sections were 0.04 m length. Simulation results show larger solid generation at the bottom section due to heavy fraction segregation. According to simulation results, heavy fractions go down during the expansion process and the IU process favoring the generation of pyrobitumen at the cell botom.

Simulation		Experiment
18%	3 cm	13%
24%	4 cm	27%
24%	4 cm	32%
34%	4 cm	29%

Figure 10. Solid mass distribution (prechar+residue) at the end of IU experiment.

Figure 11 shows the API gravity in produced oil for the difference samples taken during the IU experiment. API gravity increases when IU process is established. First two samples correspond to thermal expansion process while the third to fifth samples correspond to the step controlled by the IU process (10 – 98 hours). The reduction in the oil

production quality for the last sample is due to large heavy fraction production retained in the core at the end of the IU experiment.

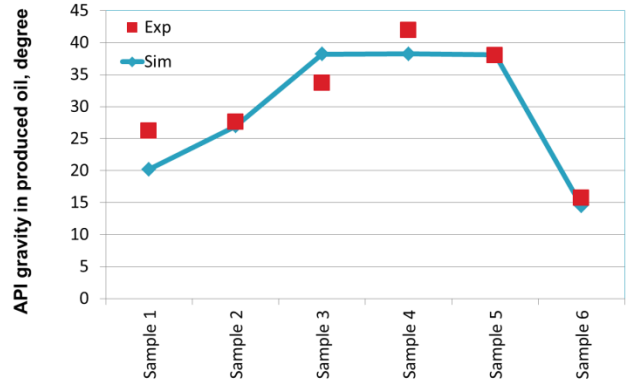


Figure 11. API gravity of produced oil per sample for the IU experiment.

CONCLUSIONS & RECOMENDATIONS

A large variety of phenomena occur during the IU process. They must be deconvoluted in order to understand separately the contribution of the different phenomena in the whole process. Performing a history matching of an IU experiment is challenged, mostly when a large number of parameters are unknown. The simulation process can help to identify which parameters are fundamental to represent properly the IU process and which ones are not essential.

A sensitivity analysis was performed to identify the effect of some parameters in the IU model based on experimental condition for the IU experiment. This analysis put major emphasis in non-well known physical properties in particular for the C14+ fraction and non-soluble oil fraction (NSOs). The sensibility analysis has permitted to identify the appropriate combination of parameters to obtain a good match between the experiments and simulation results.

Simulations results show that is feasible to reproduce experimental results for IU experiences using a reservoir model.

Three stages were identified for the IU process at lab scale. The first stage controlled by the thermal expansion of fluids and water production. A second step controlled by the IU process and the third one, controlled by the gas displacement. The in situ upgrading controlled step implies a smooth slope of hydrocarbon production (light to intermediate oil fractions), most of them in gas phase at reservoir conditions according to simulation results. This step implies a slow oil production of improved hydrocarbons.

Third step corresponds to gas injection process with the purpose to evacuate the whole liquids remained in the core.

Experimental actions should be done in order to reduce the number of uncertainties in the current IU model. A better characterization of the pseudo-components that constitutes the IU model must be done, in particular, for the heavy oil fractions. We recommend improving characterization of C14+ and NSO to reduce uncertainties in the thermodynamic model.

ACKNOWLEDGMENT

TOTAL S.A. company is gratefully acknowledged for sponsoring CHLOE's research activities.

NOMENCLATURE

X_i = reacting kinetic class, ad
 w_i =weight fraction of component X_i , ad
 x_i =molar fraction of component X_i , ad
 d_i =mass stoichiometric coefficient of component X_i , ad
 α =molar stoichiometric coefficients, ad
 d =mass stoichiometric coefficients, ad
 M_w =molecular weight, kg/gmole
 \emptyset =porosity, ad
 V =total volume, m³
 S =saturation, ad
 n =molar density, gmole/m³
 ρ =mass density, g/m³
 v =molar volume, m³/gmole
 μ_l =lamella effective viscosity, cP
 K =constant velocity, mole/day
 A =pre-exponential factor
 E_a =activation energy, kJ/gmole
 T =absolute temperature, K
 R =ideal gas constant, kJ/gmol K
 K_v =K-value, ad

Indices

β =phase (oil, gas, aqueous)
 j =j reaction
 i =i component
 P =phase number
 S_j =reactive component S_j
 N_c =number of chemical classes or pseudo-components in the model
 N_r =number of reactions
 t =total

REFERENCES

- Behar, F., Lorant, F., & Mazeas, L. (2008). Elaboration of new compositional kinetic schema for oil cracking. *Organic Geochemistry*, 39, 764-782.
- Butler, R.M. & Stephens, D.J. (1981). The gravity drainage of steam-heated heavy oil to parallel horizontal wells. *The Journal of Canadian Petroleum Technology*, April-June, 90-96.
- Constantinou, L., Gani, R., & O'Connell, J. P. (1995). Estimation of the acentric factor and the liquid molar volume at 298K using a new group contribution method. *Fluid Phase Equilibria*, 103, 11-22.
- Kristensen, M.R., Gerritsen, M.G., Thomsen, P.G., Michelsen, M.L., & Stenby, E.H. (2007). Coupling chemical kinetics and flashes in reactive, thermal and compositional reservoir simulation. *SPE Reservoir Simulation Symposium*. Houston, TX, 26-28 February.
- Kumar, J., Fusseti, L., & Corre, B. Modeling in-situ upgrading of extra-heavy oils/tar sands by subsurface pyrolysis. Paper SPE N° 149217 presented at the Canadian unconventional resources conference, Calgary, Canada, 15-17 November 2011.
- Marrero, J., & Gani, R. (2001). Group-contribution based estimation of pure component properties. *Fluid Phase Equilibria*, 183-184, 183-208.
- Peng, D.Y., & Robinson, D.B. (1976). A new two constant equation of state. *Industrial & Engineering Chemistry Fundamentals*, 15(1): 59-64.
- Riazi, M. R. (2005). *Characterization and properties of petroleum fractions*. (1st ed.). Baltimore, MD: ASTM International.
- Saber, N. & Shaw, J. (2009). Toward multiphase equilibrium prediction for ill-defined asymmetric hydrocarbon mixtures. *Fluid Phase Equilibria*, 285, 73-82.