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## **Azeotropic Heated Vapour Extraction- A New Thermal-Solvent Assisted Gravity Drainage Recovery Process**

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### **Abstract**

Thermal-Solvent Assisted Gravity Drainage processes are heavy oil recovery processes in which the stimulation mechanism for bitumen viscosity reduction is by heating and dilution. The range of the injected solvent concentration with steam may be low such as in Solvent Assisted-SAGD or very high such as in Heated Vapour Extraction. The performance behaviour of these processes is significantly driven by the complex thermodynamic interaction of steam and solvent, heat transfer, multiphase fluid equilibrium and flow in the porous medium.

ExxonMobil and its affiliate Imperial have been optimizing the existing recovery processes and developing new technologies to improve the efficiencies and environmental performance of the heavy oil production operations. Recent focus has been on developing thermal-solvent based recovery processes through an integrated research program that includes fundamental laboratory work, advanced numerical simulation studies, laboratory scaled physical modeling, and field piloting. The research program aims at in-depth investigation and understanding of process physics and mechanisms, and evaluating process performance and behaviour to enable development of new recovery methods and to enhance the performance.

This paper focuses on the fundamental concepts of Azeotropic Heated Vapour Extraction, a new thermal solvent recovery technology developed by ExxonMobil-Imperial. This technology takes the combined advantages of the solvent dilution mechanism for enhanced oil production rate with the minimum required energy (GHG emission), as well as the effectiveness of energy transport of steam to minimize the required solvent in circulation for the extraction process. In this paper, the complex solvent-steam phase behaviour and reservoir fluid flow and their interaction under operating conditions are investigated. The analysis of experimental and modeling data shows that the injection of solvent-steam mixture at its azeotropic condition results in significant improvement in process key performance indicators (KPI's). At these conditions, the reservoir is heated to the minimum boiling temperature of the solvent-steam mixture compared to a Heated VAPEX or Solvent Assisted-SAGD process resulting in the reduction of the required energy thereby minimizing the solvent-to-oil ratio. Also, due to phase equilibrium, the vaporization of in-situ water is prevented resulting in the reduction of retained solvent in the depleted zone of the reservoir. It is found that

an improvement in the process KPI's is dependent on the volatility of the selected solvent. The process KPI's also vary with operational conditions. The recovery process is optimized for certain reservoir constraints through the selection of the solvent boiling range and consequently the azeotropic steam content in the injected mixture.

**Keywords:** VAPEX, Heated VAPEX, Azeotropic Heated VAPEX, Minimum-Boiling Azeotrope, Solvent Assisted-SAGD, Solvent-Steam Phase Behaviour

## Introduction

The gravity drainage recovery process concept for bitumen extraction from Canadian oil sands was first developed by Butler in 1970s when he tested Steam Assisted Gravity Drainage (SAGD) at Imperial Oil's research center and piloted SAGD for the first time at Cold Lake (Butler 1979 and Butler et al. 1981). Currently SAGD is used commercially as one of the main in-situ recovery processes for heavy oil production in Canada. This technology currently contributes to more than 40% of the total daily in-situ heavy oil production (AER ST-53). Further to development of SAGD, Butler developed an analog process to SAGD, Vapour Extraction (VAPEX) process (Butler and Mokrys 1989), in which the injected vapour propane or butane is the working fluid for bitumen viscosity reduction. The concept behind VAPEX process was to replace a high energy intensity injectant (steam in SAGD) with a low energy intensity injectant (vapor solvent in VAPEX) for bitumen extraction (Butler and Mokrys 1989, 1991, and 1993). In this work, Butler and Mokrys (1991 and 1993) conducted a series of experiments to evaluate the effect of heating the injected vapor solvent (propane) to higher temperatures on the bitumen production rate of VAPEX process. In their experiments, both direct and indirect heating of propane was evaluated. The experimental data resulted from the testing showed that the heating of solvent in the VAPEX process can enhance the production rate of bitumen several folds. Heating of the injected solvent, condensation and release of heat of vaporization at its dew point due to temperature difference between the injected vapour and bitumen on vapour-bitumen interface, results in heating and slight viscosity reduction in the bitumen, and forming a drainage bank of condensed solvent on interface, which can significantly improve the dispersive and diffuse mixing of solvent with bitumen that enhances the production rate of the process compared to lower operating temperatures.

Use of light hydrocarbon solvents such as propane or butane for Heated VAPEX has some thermodynamic and phase behaviour limitations that impacts the optimal performance of the process. Use of heavier hydrocarbon solvents at a certain thermodynamic state mixed with steam improves the recovery performance of the Heated VAPEX process that is the subject of this article.

ExxonMobil and its affiliate Imperial Oil have been investigating solvent based thermal recovery technologies through an integrated research program that includes fundamental laboratory work, advanced analytical and numerical simulation studies (Dickson et al., 2013b, Khaledi et al., 2015, Mensah-Dartey et al., 2015, Motahhari and Khaledi, 2018), laboratory scaled physical modelling (Khaledi et al., 2012) and field piloting (Khaledi et al. 2014, Dickson et al., 2013a, Dittaro, et al., 2013, Perlau et al., 2011). This research program is a part of the initiative to develop, improve and commercialize in-situ recovery technologies (Boone et al, 2014, Boone et al, 2011). Learnings of physical modeling experiments, field pilots and commercialization of three thermal recovery technologies (i.e. SAGD, SA-SAGD, and Liquid Addition to Steam for Enhancing Recovery (LASER) (Leaute, 2002, Stark 2013)), are all incorporated into this research program. The program aims at in-depth understanding of process physics and mechanisms, evaluating process performance and behavior, and developing new thermal solvent recovery processes.

Recently, the focus of the research program has been to develop High Temperature Multicomponent Solvent Vapour Extraction (HTMS-VAPEX) and its enhanced variations such as Azeotropic HTMS-VAPEX (AHTMS-VAPEX) processes (Khaledi et al. CA-2886479-2013, Khaledi et al. CA-2857329-2014, Boone et al. CA-2915571-2015, Khaledi and Motahhari, CA 2972068-2017). In AHTMS-VAPEX process an optimum volume of steam is co-injected with hydrocarbon solvent in the vapor phase. Development of

this technology enables an environmentally and economically viable bitumen recovery from Alberta's in-situ resources. The research program includes laboratory testing, simulation studies and a field trial. The aim is to understand the process physics and mechanism, evaluate process behaviors, and optimize the performance. AHTMS-VAPEX is a solvent based recovery process that minimizes the use of fresh water compared to thermal recovery processes. It is an energy efficient oil recovery process requiring far less thermal energy compared to steam based recovery processes (e.g. SAGD and Solvent Assisted-SAGD), consequently reducing the required natural gas for thermal energy generation and Greenhouse Gas (GHG) emissions. Moreover, AHTMS-VAPEX is an ultra-low to medium pressure (300-3000 kPa) recovery technology applicable not only to SAGD resources, but also to very shallow and low pressure reservoirs where currently no commercial technology is applicable. The ultra-low pressure nature of this recovery technology results in reduced risk of fluid escape to the surface which could be experienced in high pressure in-situ recovery processes.

In this paper, the thermodynamic properties including asphaltene/heavy liquid phase formation tendency of the hydrocarbon solvents applicable to Heated VAPEX process and their suitability for this process is evaluated. The azeotropic behaviour of the steam and solvent at the operating conditions of Azeotropic Heated VAPEX is discussed and the effect of azeotropic behaviour on the phase equilibrium of the reservoir fluid and process performance has been analyzed. Based on the analysis of azeotropic behaviour, a method for selecting an optimal fraction of steam and solvent for co-injection in the Azeotropic Heated VAPEX process has been developed. As discussed in this paper, the key advantages of this methodology are significant reductions in the solvent-to-oil ratio (SolOR) relative to solvent-only heated vapour injection (referred to as Heated VAPEX) and reduction in solvent storage and improvement in produced bitumen-to-retained solvent ratio (PBRSR). In the presented work, the focus of the study is optimization of the key performance indicators of the Azeotropic Heated VAPEX process from the technical perspective. The economics of the recovery process and consideration for solvent type, solvent recovery unit design, and surface facility operating and capital cost differences has not been discussed in this work. The authors summarise the discussion on economics that, with the achieved KPI's enhancements in AHTMS-VAPEX and its associated plant capital and operating costs, the economics of this recovery technology is significantly more attractive than the other variations of Heated VAPEX recovery process.

In the context of this paper, the developed recovery process concept in which azeotropic mixture of solvent-steam is used as injected vapour is referred to as Azeotropic Heated VAPEX, and the process in which the injected vapour is 100% solvent is referred to as Heated VAPEX in general. Also, when the injected solvent is a multi-component solvent such as a commercial diluent, the corresponding recovery processes are referred to as AHTMS-VAPEX and HTMS-VAPEX processes with and without optimal steam co-injection, respectively.

## Process Thermodynamics

The solvent thermodynamic properties and its phase behaviour have a significant role in performance of Heated VAPEX process and in general solvent assisted thermal recovery processes (Khaledi et al. 2015). In this section a close look is given to thermodynamic properties of hydrocarbon solvents, solvent-bitumen asphaltenes precipitation behaviours and solvent-steam phase behavior and their impact on the Heated VAPEX process performance. Based on these analyses, the Azeotropic High Temperature Multicomponent Solvent Vapour Extraction (AHTMS-VAPEX) recovery process is developed and range of suitable solvents for this process are selected. AHTMS-VAPEX is a variation of HTMS-VAPEX and in general Heated VAPEX process in which an optimum fraction of steam is co-injected with a multi-component hydrocarbon solvent in vapor phase. The optimum fraction of steam for a given solvent is determined according to azeotropic phase behavior which is discussed in details in this section.

### Solvent Selection-Thermodynamic properties and Asphaltene Behaviour

The commercially available solvents for Heated VAPEX process can range from light hydrocarbons such as propane and liquefied petroleum gas (LPG) to heavy fractions such as gas condensates and different refinery naphtha streams. The readily available solvent in Athabasca region is gas condensate/naphtha (diluent) that is used as diluting solvent for bitumen pipeline transportation. In the following analysis, for simplicity the pure hydrocarbon compounds are used to introduce the fundamental phase behaviour of the hydrocarbon solvents, then the analysis is extended to the solvent mixtures.

Figure 1 shows the saturation vapor pressure of a number of alkanes that are the main constituents of aforementioned hydrocarbon solvent mixtures. As it can be seen from this figure, the vapor pressure of the solvents increases as the solvent become lighter. The operating temperature range of interest in Heated VAPEX process is 70-150 °C in which the bitumen viscosity is reduced enough to provide an effective dispersive and diffusive mixing and therefore sufficiently high bitumen recovery rates. In this temperature range, light hydrocarbons such as propane or butane approach the higher limits of operating pressures for oilsands reservoirs as shown in dotted envelop in Figure 1. Figure 2 shows the enthalpy of the hydrocarbon solvents. As it can be seen, the heat of vaporization of the solvents decreases as the temperature increases and approaches to the critical temperature. For the operating temperature range of interest in Heated VAPEX process, lighter hydrocarbons have the lowest heat of vaporization. This translates into a higher volumes of solvent in circulation (in cold liquid equivalent) or solvent-to-oil ratio (SolOR) in the Heated VAPEX process. For most of shallow Athabasca reservoirs, the maximum operating pressure is limited by depth of reservoir, as well as geological limitation such as low pressure water or gas thief zones. Therefore, the lighter solvents have smaller pressure and temperature operating windows for use as effective solvents for Athabasca reservoirs.

The lighter hydrocarbon solvents also pose the issue of the second heavy liquid phase formation and/or asphaltene precipitation which results in porous medium and near wellbore plugging and permeability impairment. Use of lighter solvents can also result in loss of a significant recoverable bitumen volumes due to deposition of the heavy phase in the depleted reservoir. Figure 3 shows the second heavy liquid phase or asphaltene precipitation behavior of a typical Athabasca bitumen with different solvents at a solvent content of 70 wt% and two different temperatures. As it is seen, a greater portion of bitumen partitions to the second heavy liquid phase from a mixture of lighter solvents and bitumen in comparison to the mixtures of heavier compounds and bitumen. In fact, the second heavy liquid phase formed by lighter hydrocarbon solvents such as propane and butane not only contain the asphaltene portion of the bitumen, but also a substantial valuable portion of the non-asphalt heavy end molecules of the bitumen. Whereas, the heavier compounds such as pentane, hexane and heptane only precipitate a portion of asphaltene from the bitumen. It is also noted that an increase in temperature does not reduce the fraction of the second heavy liquid phase substantially for lighter solvents (C3 and C4), whereas for heavier solvents, an increase in temperature noticeably reduces the asphaltene precipitation tendency. Although, this characteristic may provide higher quality of upgraded heavy oil product, it results in loss of unrecoverable heavy oil resource in the form of deposited heavy-ends in subterranean reservoir. Therefore, from the recovery process performance perspective, heavier solvents are preferred for Heated VAPEX process as a small proportion of the bitumen is retained in reservoir in the form of an asphaltene phase resulting in less recoverable bitumen volume loss. The preferred level of deasphalting for producing an upgraded bitumen product is at the level of 4-8%. Experimental physical modeling studies in the laboratory, as a part this research program, has indicated that the Heated VAPEX process using C3 and C4 as a solvent retains a significant amount of bitumen as a viscous unrecoverable second liquid phase in the reservoir. Furthermore, propane does not form an azeotrope with steam, which is considered as an advantage to improve the performance of process. Azeotropic steam content of butane is also very small resulting in an insignificant process performance improvement as it will be discussed in this paper.

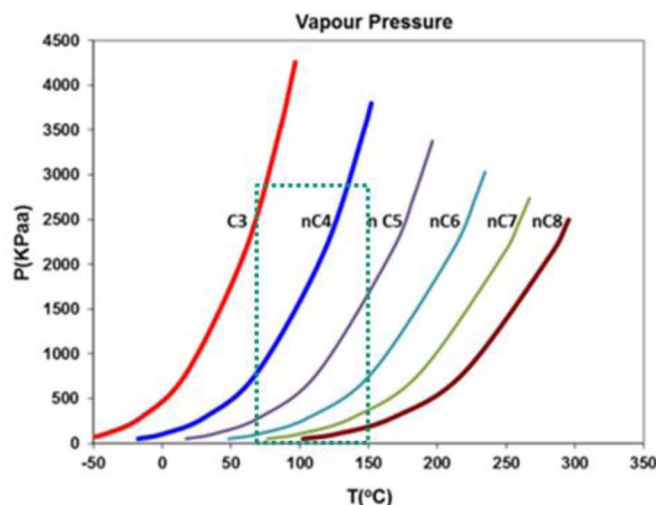


Figure 1—Vapor pressure of normal hydrocarbons solvents

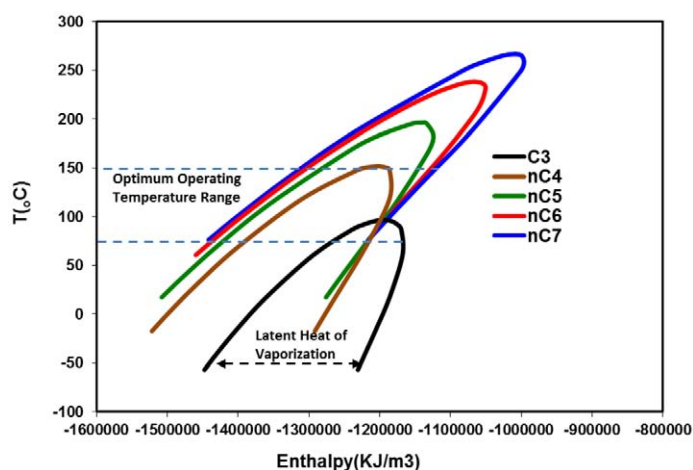


Figure 2—Latent heat of vaporization/condensation of normal hydrocarbons solvents

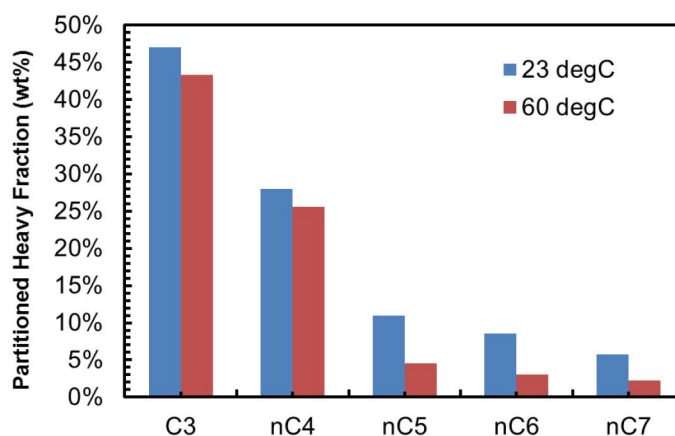


Figure 3—Fractional partitioning of Athabasca bitumen to the Asphaltene/heavy hydrocarbon liquid phase with normal hydrocarbon solvents at 70wt% solvent fraction.

### Solvent Selection-Solvent-Steam Azeotropic Behaviour

In this section, the condensation behavior of solvent-steam mixture and its effects on Heated VAPEX and Azeotropic Heated VAPEX process mechanism is studied. The pure compounds are used to illustrate the conceptual behavior of the solvent-steam system. The multicomponent hydrocarbon mixture solvents



behave fundamentally similar to single component hydrocarbon solvents. The phase behavior of solvent mixtures with steam is superposition of individual pure compounds behaviors present in the mixture. The azeotropic phase behaviour analysis of a solvent-steam system is extended to multicomponent hydrocarbon mixture solvents such as commercially available diluents.

Most of hydrocarbon compounds with partial pressures relatively close to steam at a certain temperature range exhibit positive deviation from ideality and Raoult's law. In such cases, the actual partial pressure of each component is larger than its calculated partial pressure from Raoult's law in the ideal system. This is shown in a P-x diagram for the n-hexane and steam system in Figure 4. As it is seen, the actual partial pressures of n-hexane and steam are larger than the ideal partial pressures of these compounds from Raoult's law. This non-ideal behavior of n-hexane and steam mixture results in actual total pressure larger than ideal total pressure at certain temperature; with a positive deviation from ideality. In a constant pressure system, this positive pressure deviation behavior transfigures into azeotropism with minimum-boiling temperature characteristics. This behavior is shown in Figure 5 on the T-xy diagram for the n-hexane and steam system with a minimum-boiling temperature azeotrope of 182 °C at  $x=y=0.64$ . This vapor-liquid equilibrium diagram shows that vapor is at equilibrium with essentially liquid water at concentration ranges less than azeotrope, (nC6 in vapor phase (y) is 0 to 0.64 and in liquid phase (x) is less than 0.02). For n-hexane vapor concentrations higher than the azeotrope, ( $y>0.64$ ) the vapor is at equilibrium with essentially liquid n-hexane ( $x>0.92$ ).

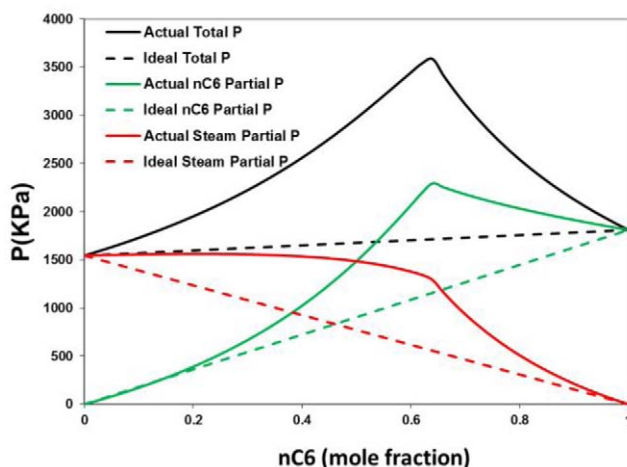


Figure 4—P-x diagram comparing ideal and actual partial pressure for n-hexane-steam system at 200 °C.

Depending on the recovery process in which the solvent-steam mixture is injected, the injected solvent concentration can be on either side of the azeotropic point. In the SA-SAGD process, the solvent concentration is on the lower end range which is typically 0.6-6 mole % (5-30 LVE%; liquid volume equivalent). This falls on the left hand side region of the azeotrope point, shown in Figure 5. For the Heated VAPEX process using 100 % solvent, the injected solvent concentration falls on the right hand side of the azeotrope point.

If the solvent-steam mixture is injected at the SA-SAGD conditions, the saturation temperature of injected steam drops to some extent due to mixing with solvent; as shown in Figure 5 with point "a". As the mixture of solvent and steam travels in the vapor chamber approaching the vapor-bitumen interface, it condenses and delivers heat of condensation and the vapor saturation temperature decreases. This is shown in Figure 5 on the dew point curve (point "a" to "b") on the left hand side of azeotrope point. In this region, the condensing compound from the vapor mixture is essentially pure water. The concentration of n-hexane in the vapor phase increases as steam condenses. This trend lasts until most of steam is condensed and the solvent concentration in vapor has reached the azeotrope concentration ( $y=0.64$ ) where n-hexane begins to

co-condense with steam (point "b" in Figure 5). The phase behaviour of solvent-steam system injected at the operating conditions of SA-SAGD process and its effects on the SA-SAGD performance is discussed in details by [Khaleedi et al. 2015](#).

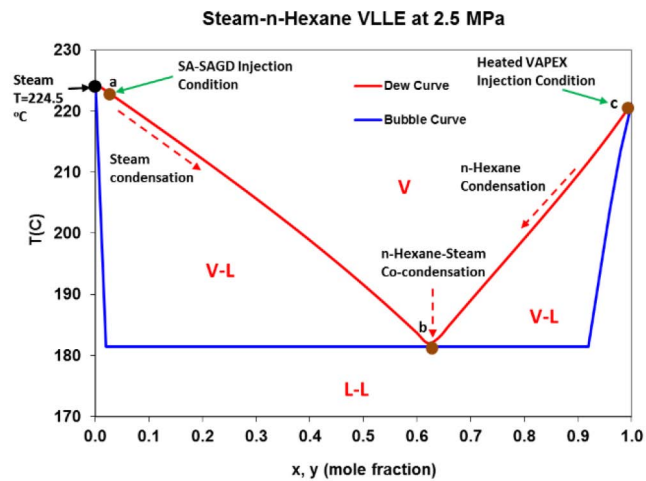


Figure 5—T-xy diagram for n-hexane-steam system, minimum-boiling temperature azeotrope at 2.5 MPa.

If the n-hexane concentration is 100% such as in Heated VAPEX process, the solvent condensation curve follows the dew point curve on the right hand side of azeotropic point (point "c" in Figure 5). When the solvent-steam mixture loses heat and is cooled, first the n-hexane condenses until the mixture composition reaches azeotropic point "b", where both n-hexane and steam begin to co-condense.

All other hydrocarbon solvents that are present in commercial diluents with volatility close to nC6 follow the same azeotropic characteristic. Figure 6 demonstrates the collective dew point curves and azeotropic points of vapor mixtures of a number of n-alkane solvents with water at 1 MPa pressure. As shown in this figure, propane (C3) is an exception and does not form an azeotropic mixture with steam; hence, the minimum dew point temperature of its mixture with steam is equal to the saturation temperature of propane. As a consequence, all co-injected steam with this solvent will condense first, then C3 begins to condense. Therefore, the effective saturation temperature, and in a recovery process, the operating temperature of the recovery process with this solvent is the saturation temperature of the propane at the operating pressure. Other medium and heavy molecular weight hydrocarbons present in diluent form minimum boiling-temperature azeotropic mixtures with steam in the vapor phase as shown for nC4 to nC9 in Figure 6. The near-azeotropic mixture of any of these solvents with steam will travel through the depleted chamber to the recovery interface and will condense at the azeotropic temperature and concentrations. Butane (nC4) also forms an azeotropic mixture with steam, however, the azeotropic content of the steam is a small fraction (~1 CWE Vol%) resulting in an insignificant improvement in the efficiency of the injected mixture in Azeotropic Heated VAPEX process as will be discussed further in the next section. Due to this reason, and other thermodynamic limitations that were discussed earlier, propane and butane are not considered effective solvents for the Azeotropic Heated VAPEX process.

The implication of the azeotropic phenomena on the Heated VAPEX process and the conceptualization of Azeotropic Heated VAPEX process and its advantages over the Heated VAPEX process is further discussed in the next section.

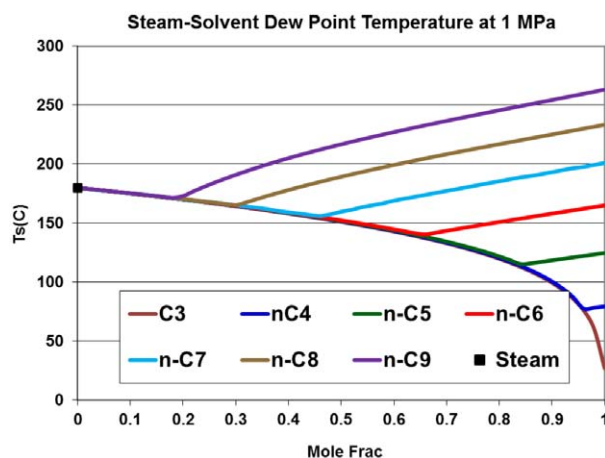


Figure 6—Ty diagram for solvent-steam system at 1 MPa, minimum-boiling temperature azeotrope.

### Azeotropic Heated VAPEX Process Conceptualization

In the Heated VAPEX process, in which the injected solvent concentration is 100%, the condensation curve follows the dew point curve on the right hand side of azeotropic point in Figure 5 as discussed previously. However, with the absence of water in the injected vapor, the solvent begins to vaporize the existing in-situ water in the reservoir porous media, to create an equilibrium condition in which the amount of vapor water in the gas phase is equivalent to the mole fraction of water in the azeotropic condition. The vaporization of the in-situ water, includes the irreducible and a large fraction of the bound water in the depleted chamber. Simultaneously, the solvent gradually condenses in the vapor chamber to provide the required heat of vaporization for vaporizing the in-situ water. The vaporization of water and condensation of the solvent continues as the chamber volume expands. This thermodynamic phenomenon increases the solvent-to-oil ratio (SolOR) for Heated VAPEX and therefore reduces the efficiency of the process. The condensation of the solvent in the depleted chamber also increases the solvent retention during the steady-state conditions. Furthermore, the injection temperature of 100% solvent vapor is the saturation temperature of the solvent which is above the azeotropic temperature. For example, in case of n-hexane injection at 2.5 MPa shown in Figure 5, the injection temperature is 220 °C. However, the condensation of vaporized in-situ water and solvent occur at azeotropic condition at 182 °C on the vapor bitumen interface where the drainage mechanism is taking place. As a result, a significant volume of the reservoir rock will be unnecessarily heated to temperatures as much as 220 °C which is an additional heat sink compared to injection at the azeotrope temperature of 182 °C ( $\Delta T = 38$  °C). With the vaporization of in-situ water, a desiccated region will develop around the injector which is nearly completely water free. It is possible that this could be advantageous in some circumstances. However, it could also be a significant disadvantage due to factors such as salt or scale deposition and fines migration, causing pore plugging and a shift from a water wet to an oil wet rock system resulting in less favorable residual oil saturations and oil relative permeabilities.

The azeotropic behaviour described above can be exploited to improve the performance of the process. A key feature of the azeotropic phenomena is that, if the vapor solvent-steam mixture is injected at the azeotropic condition, the two compounds behave as a single fluid. That is both fluids condense together in the same molar ratios of concentrations as they exist in the vapor. Additionally, there is no tendency for either compounds to preferentially vaporize from the liquid state into the vapor state (i.e. vaporize additional in-situ water) or condense from the vapor state into liquid state (i.e. condensation of solvent in depleted chamber) and they will co-condense at the bitumen interface where mixing with bitumen and drainage process is taking place. As such, the combined fluids can behave effectively as a single compound with modified properties compared to either of single compounds. Therefore, when the solvent-steam vapour mixture is injected at or near its azeotropic condition, the vaporization of in-situ water and condensation of the solvent in the depleted chamber is prevented.



Additionally, steam is a very effective working fluid for transferring heat whereas hydrocarbon solvents tend to be relatively inefficient working fluids for that purpose. The heat of condensation of hydrocarbons is about 10% of the heat of condensation of steam. Conversely, hydrocarbon solvents are very effective viscosity reducing agents for heavy oils whereas water is practically immiscible. However, mixtures of hydrocarbons and water at the azeotrope behave largely as a single fluid with beneficial qualitative features of both the water and the hydrocarbon solvent.

Based on the discussion above, an optimal injection ratio of solvent and steam is a ratio that is at or close to the azeotropic concentration for the solvent-steam vapor mixture. Practical implications of this optimizing approach are partly illustrated by the results of the analyses given hereafter. The n-hexane-steam system which was previously discussed is given as an example for analysis of enthalpy content of the azeotropic mixtures. Considering mixture of n-hexane-steam injection at 2.5 MPa, as shown in Figure 5, the molar fraction of solvent at the azeotrope is approximately 64% so that the water molar fraction is 36%. On mass basis this converts to a 10.5% water fraction and on a volumetric basis this converts to a 7% water volume fraction. The heat of vaporization of hexane at the azeotrope temperature is 220 kJ/kg and that for water is 2000 kJ/kg. The combined fluids have an effective heat vaporization of about 407 kJ/kg of mixture. As a result the amount of azeotropic fluid required to deliver the same heat to the reservoir is 54% less on mass or 48% on the liquid volume basis compared to solvent only, thus the operating solvent-to-oil ratio is reduced by 48 %. The operating pressure and solvent volatility affect the azeotropic mole fractions and therefore the energy content of the azeotropic mixture of solvent and steam, however the described behaviors and mechanism remain similar. The results of the enthalpy calculation described above are given in Table 1 for a number of solvents. This table shows the azeotrope temperatures and molar concentrations for pentane, hexane and heptane at 1 MPa and 2.5 MPa pressures. It also provides mass fractions, standard volumetric fractions and enthalpies for steam and solvent at their respective, ideal partial pressures for the azeotrope temperature. It can be seen from Table 1 that the azeotrope molar concentration of steam increases significantly from lighter to heavier solvents. However, for a given solvent, there is small variation in azeotrope molar concentrations with pressure. It can also be seen from Table 1 that the heat of vaporization for the combined fluids increases much more substantially for heavier solvents at the azeotrope than it does for the lighter solvents. Therefore, the SolOR reduction of the process due to azeotropic concentration of the injection vapor mixture increases as the solvent become heavier, which is illustrated in Table 1. In all cases the required solvent in recirculation for bitumen extraction is significantly reduced. For pentane it is estimated to be about a 23% reduction at 1 MPa. The benefit is predicted to increase with pressure and with the use of heavier solvents. The required solvent recycling is expected to be reduced by 50% or more for heavier solvents as will be discussed in more details in the next section using reservoir simulation study.

**Table 1—Properties for Steam and hydrocarbon solvents and azeotropic conditions.**

Design Parameters		Azeotropic Properties			Steam-Solvent Ratios				Thermal Properties			
Solvent	Pressure (Mpa)	Temperature (°C)	Steam Mole Fraction	Solvent Mole Fraction	Steam Mass Fraction	Solvent Mass Fraction	Steam Volume Fraction	Solvent Volume Fraction	Steam Heat of Vaporization (KJ/Kg)	Solvent Heat of Vaporization (KJ/Kg)	Combined Heat of Vaporization (KJ/Kg)	SolOR Reduction (%)
nC5	1.0	116.0	0.16	0.84	0.045	0.955	0.029	0.971	2213	319	405	23
nC6	1.0	140.5	0.34	0.66	0.097	0.903	0.066	0.934	2142	270	452	42
nC7	1.0	155.7	0.54	0.46	0.174	0.826	0.125	0.875	2095	226	551	61
nC5	2.5	157.7	0.20	0.80	0.059	0.941	0.038	0.962	2089	208	318	36
nC6	2.5	182.0	0.36	0.64	0.105	0.895	0.071	0.929	2006	220	408	48
nC7	2.5	196.9	0.54	0.46	0.174	0.826	0.125	0.875	1951	210	513	61

The analysis described in the previous sections for the pure compounds are used to illustrate the conceptual behavior of the solvent-steam system. The phase behavior of multicomponent hydrocarbon mixture solvents such as commercially available diluents is more complex than the pure compounds and is not detailed in this paper, however in essence, same vapour-liquid phase equilibrium and condensation enthalpy behavior is observed when they are mixed with water in the vapor phase. In this case, the effective properties of the solvent mixture can be considered as superposition of individual pure compound behaviors. Figure 7 show the dew point curve and minimum boiling point (semi-azeotropic) behaviour of a typical commercial diluent and steam mixture. Figure 8 presents the vaporization/condensation enthalpy of diluent and its mixture with steam at azeotropic condition. As it can be seen, this mixture behaves closely to hexane and heptane having the boiling range similar to these pure compounds.

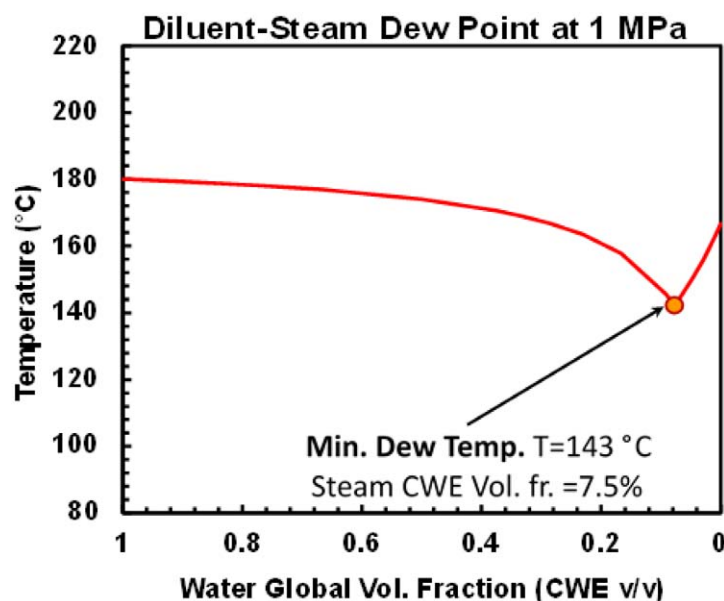


Figure 7—Minimum boiling pint (semi-azeotropic) behavior of steam-multicomponent solvent (diluent).

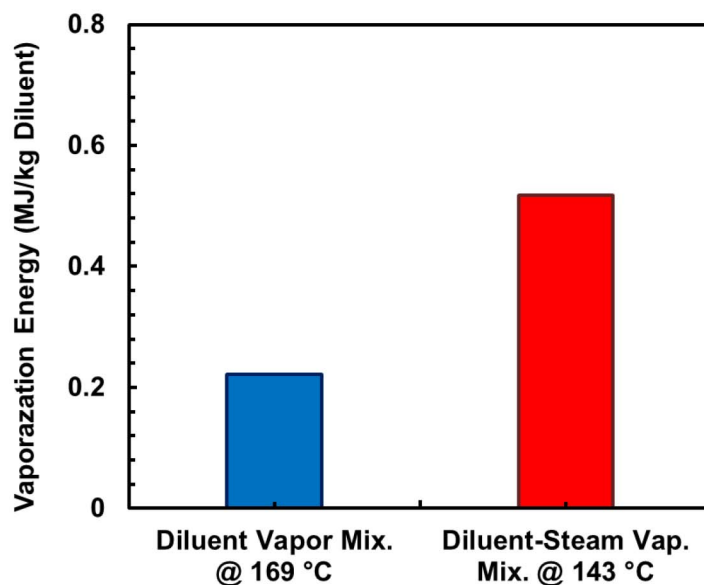


Figure 8—Vaporization enthalpy of diluent and diluent-steam at minimum boiling point and 1 MPa.

## Azeotropic Heated VAPEX Concept Validation and Performance Analysis-Numerical Simulation Modeling

In this section, reservoir simulation modeling is used to validate the Azeotropic Heated VAPEX recovery process concept and to quantitatively assess the enhanced performance of this process compared to the Heated VAPEX process. The study includes evaluation of the Azeotropic Heated VAPEX for pure compound solvents in order to illustrate the process physics. Also, the quantitative process performance analysis of Azeotropic High Temperature Multicomponent Solvent VAPEX (AHTMS-VAPEX) recovery process with commercial multicomponent solvent mixture (diluent) is presented. An in-house fully-implicit thermal-compositional reservoir simulator, EMPower™ (Lu et al., 2008) was used to provide a physics-based platform for physical, thermal, chemical, and phase equilibrium modeling of multi-phase fluid flow in porous media associated with the Azeotropic Heated VAPEX process.

### Reservoir Model Description

The simulation model used for this study is a 2-D corner-point half-symmetry reservoir model. The dimension of the half-model along the well-pairs is 1000 m, the well spacing is 140 m and the pay thickness is 30 m. The grid cell dimensions are  $1 \times 1000 \times 1$  m in i, j, k directions. The production well stand-off is 2 meter above the base of the reservoir and the injection well is located 5 m above the production well. To exclude the effect of reservoir heterogeneity on simulation results, the model is populated homogenously with average generic geological properties of McMurray formation in Athabasca area. The relative permeability sets for gas-oil and oil-water systems in the simulation model are based on the measured relative permeability data. The heat transfer and losses to the over-burden and under-burden are also accounted for. The performance of the simulation model for the base SAGD process is validated against publically available production data.

It is worthwhile to note that the simulation model grid size of  $1 \times 1$  m in 2-D is relatively coarse and does not accurately model the effect of diffusion and physical dispersion and does not resolve the mass transfer boundary layer. In most of the field scale solvent based recovery simulation models, the numerical dispersion is the dominant mixing phenomena due to coarseness of the simulation grids. Neglecting the numerical mixing effects in the simulation model may result in over-prediction of solvent based recovery process performance depending on the size of the grids used in the simulation model. To overcome this limitation, a proprietary methodology has been employed in the simulations to compensate for enhanced numerical dispersion due to grid size effects. The accuracy and applicability of this methodology for solvent based recovery processes have been validated at different operating conditions against the physical model experimental data and field performance data.

The phase behavior of reservoir and injection fluids are modeled by utilizing K-values to predict phase partitioning between the gas, liquid and aqueous phases. The dead bitumen is represented by one pseudo-component in the liquid phase. The bitumen properties are generic to the Athabasca area with density of  $1017 \text{ kg/m}^3$  and viscosity of  $4 \times 10^6 \text{ mPa.s}$  at reservoir condition.

The considered solvents for the mechanistic study of Heated VAPEX and Azeotropic Heated VAPEX process physics and proof of concept are pure n-pentane and n-heptane. For performance evaluation of AHTMS-VAPEX a commercial diluent which is represented as mixtures of paraffinic hydrocarbon compounds is used. The K-values for these paraffinic hydrocarbons are based on available VLE data. The K-values for methane and carbon dioxide used in the thermodynamic models were regressed against available experimental solubility data of these components in water and bitumen. The  $\text{CO}_2$  generation by Aquathermolysis reaction is also modeled in this study.

The viscosity of the injected solvents in liquid phase were modeled using analytical correlations regressed against available viscosity data. The experimental viscosity data for bitumen-solvent mixtures exhibit excessive deviation from ideal behavior; hence, simple linear mixing rules such as Arrhenius mixing rule

cannot truly apply to these mixtures. A proprietary non-linear mixing rule is developed and implemented in the EMpower™ simulator which is proven to accurately predict the viscosity of bitumen-solvent mixtures. The accuracy of the mixing rule predictions are evaluated against an extensive set of experimental viscosity data of solvent-bitumen mixtures and are found to be within the uncertainty of the measurements. For the light components such as methane and carbon dioxide, the effective viscosity values in liquid phase are assigned to correctly match the available viscosity data of the live bitumen systems.

The constraint on the injection well is set as constant injection pressure. The injected vapor mixture quality is set as 100% at downhole injection point at its saturation temperature for all simulation cases. This downhole fluid thermodynamic condition is determined based on the wellbore heat loss modeling and pressure drop calculations for two phase flow system. It is worthwhile to note that, despite the heat losses from the wellbore, the downhole injection fluid state is a saturated vapor due to pressure drop along the injection tubing. The details of injection wellbore modeling is beyond the scope of this paper and is not discussed here. The production well is constrained by controlling the total production rate to maintain a liquid level at midpoint between the injector and producer wells using a well management logic program imbedded in the simulation model. This set of the well constraints assured that the performance of the simulation cases is not hindered by limitation on the injection and productions rates and any variations in operational pressure. All the studied simulation runs started with a 90-day preheating period to establish thermal and hydraulic communication between the injector and producer wells.

### Numerical Modeling Results

The Azeotropic Heated VAPEX process concept theorized and developed in the previous sections is examined by the numerical simulation model that is described above. The single component solvents are used to illustrate the fundamental behaviour of in-situ water vaporization, as well as the effect of solvent boiling point on the SolOR improvement in Azeotropic Heated VAPEX compared to Heated VAPEX. Also, the effect of solvent boiling point on the produced bitumen-to-retained solvent ratio (PBRSR) is evaluated using the single component solvents simulation sensitivities. Furthermore, the performance of AHTMS-VAPEX using a commercial multicomponent diluent is analyzed using the simulation model.

**Single Component Solvents-Process Mechanism.** Figure 9 shows bitumen production rate and steam-to-oil ratio (SOR) performance of a SAGD and bitumen production rate of a Heated VAPEX process with single component solvent (n-C5) for validation and comparison purpose. As it can be seen, the simulation model predicts a typical SOR and rate performance for SAGD in Athabasca reservoir. The rate performance of Heated VAPEX is superior compared the SAGD production rate at the same operation pressure, as shown in Figure 9.

Figure 10 illustrates the reservoir properties map for the Heated VAPEX simulation case with a single component solvent (n-C5) and Azeotropic Heated VAPEX at the same operating pressure. It is noted from the water saturation map that in Azeotropic Heated VAPEX, the co-injected steam at the azeotropic concentration, inhibited the vaporization of the initial in-situ water; whereas in the Heated VAPEX process, the in-situ water is completely vaporized driving the liquid water saturation to zero in the depleted chamber. It is also noted in the temperature map that the average temperature in the depleted zone for Azeotropic Heated VAPEX is lower than the Heated VAPEX. The co-injection of steam at azeotropic concentration in the Azeotropic Heated VAPEX results in the SolOR improvements compared to Heated VAPEX for both nC5 and nC7 solvents as shown in Figure 11. As it was described in the previous section, the azeotropic systems for heavier solvents have a higher energy content in the injected azeotropic fluid compared to lighter solvents and therefore result in a higher reduction in SolOR as is shown in Table 1 and Figure 11 which compares the nC5 and nC7 solvents performance.

The steam co-injection at azeotropic concentration and the related phase equilibrium changes in the Azeotropic Heated VAPEX process result in the PBRSR improvements compared to Heated VAPEX as

shown in Figure 12. In the Heated VAPEX conditions, the vaporized in-situ water in the depleted zone is replaced with hydrocarbon liquid phase which is mainly the condensed liquid solvent. Inhibiting the in-situ water vaporization in the Azeotropic Heated VAPEX results in reduction in solvent condensation in the depleted chamber which is needed to provide the required energy for water vaporization. Consequently, it minimizes the liquid hydrocarbon phase in the depleted chamber and therefore results in a reduction in solvent retention in the depleted reservoir. This is noted in the nC5 mole fraction and liquid phase saturation map in Figure 10 as a reduced residual liquid phase saturation region within depleted chamber in the Azeotropic Heated VAPEX compared to Heated VAPEX. Figure 12 shows the reduction in solvent retention in the reservoir in terms of increase in PBRSR. It is noted that Azeotropic Heated VAPEX with nC7 results in a higher increase in PBRSR compared to Azeotropic Heated VAPEX with nC5 solvent. This is due to the fact that the solvent retention in chamber is the combination of retained liquid and vapor solvent. The nC7 azeotropic vapor mixture has a lower azeotropic solvent concentration compared to nC5 azeotropic vapor mixture; hence, it has a lower vapor solvent storage in the chamber and a higher reduction in PBRSR. The bitumen recovery rates in the Azeotropic Heated VAPEX and Heated VAPEX process are generally similar as shown in recovery rate plots in Figure 13.

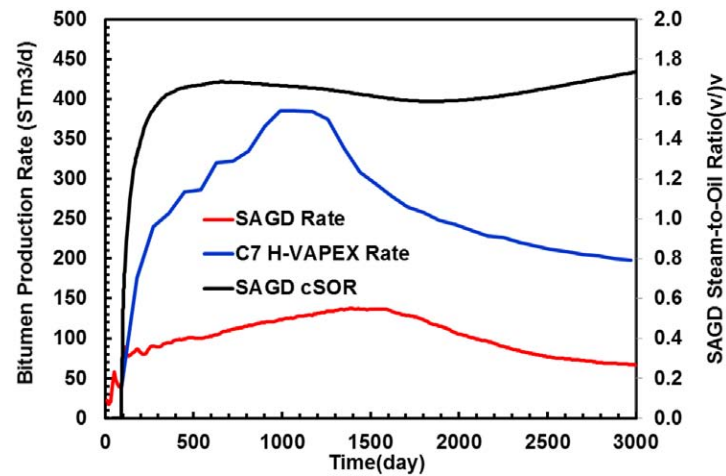


Figure 9—Comparison of production rate between SAGD and Heated VAPEX (nC7 solvent) processes at 1MPa operating pressure.

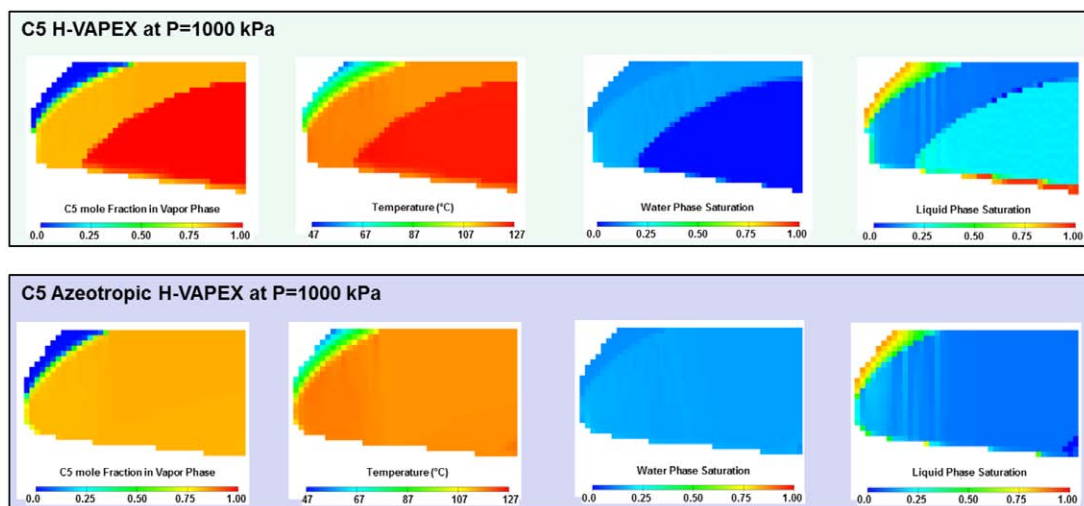


Figure 10—Comparison of reservoir properties map in Heated VAPEX and Azeotropic Heated VAPEX processes for nC5 and nC7 solvents.



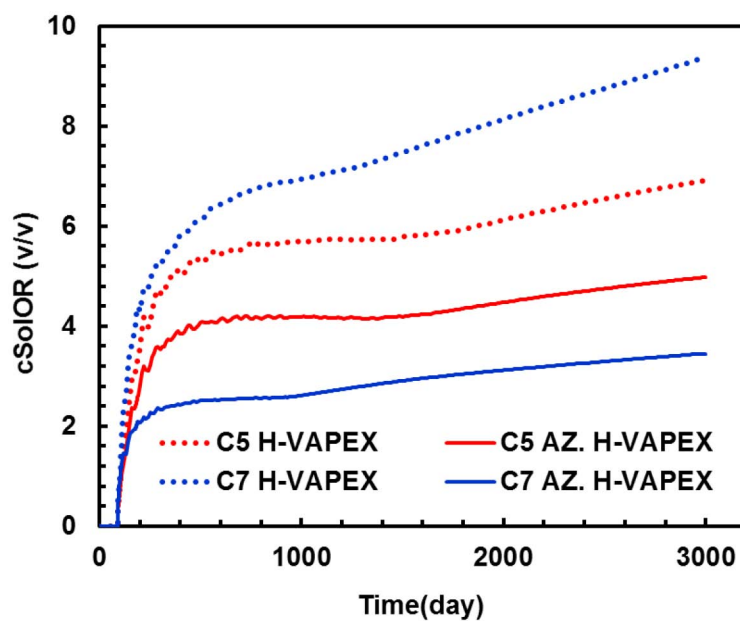


Figure 11—Comparison of SolOR between Heated VAPEX and Azeotropic Heated VAPEX processes for n-C5 and nC7 solvents at 1 MPa operating pressure.

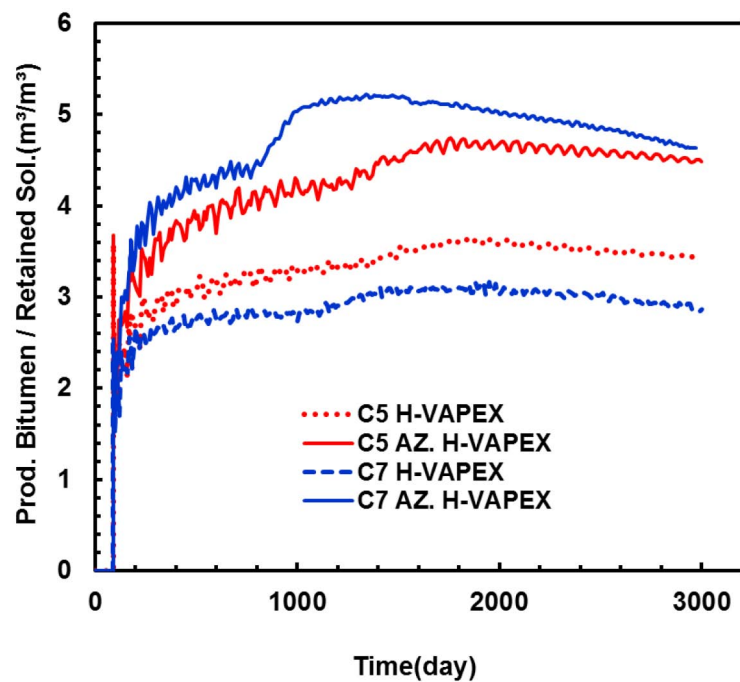


Figure 12—Comparison of produced bitumen-to-retained solvent ratio between Heated VAPEX and Azeotropic Heated VAPEX processes for n-C5 and nC7 solvents at 1 MPa operating pressure.

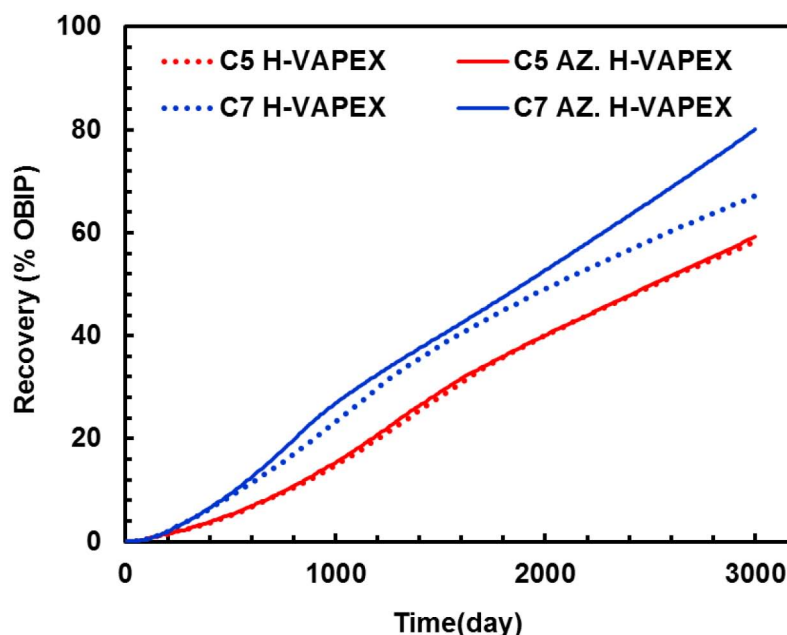


Figure 13—Comparison of bitumen recovery rate between Heated VAPEX and Azeotropic Heated VAPEX processes for n-C5 and nC7 solvents at 1 MPa operating pressure.

**Azeotropic High Temperature Multicomponent Solvent-VAPEX (AHTMS-VAPEX).** For the field applications, the commercially available solvents are mixtures of hydrocarbon compounds rather than a pure single compound. Commercial gas condensate, diluents, and naphtha are among the most commonly used solvents. The phase behavior of these multicomponent solvents with steam is much more complicated than the single component solvents. However, their phase behavior when mixed with steam can be considered as superposition of individual pure compounds behavior. These systems exhibit a semi-azeotropic behavior with a minimum boiling characteristic similar to single compound solvents as it was discussed in the previous sections (Note Figure 7). At the reservoir operating conditions, the compounds in the multicomponent hydrocarbon mixture (diluent) preferentially condense based on their relative volatility as they approach the bitumen vapor interface. Therefore, the vapor-liquid system at equilibrium in the chamber can be visualized as semi-azeotropic vapor-liquid equilibrium system of heavier compounds (higher boiling range) and water vapor at the vicinity of the injection point which gradually becomes a semi-azeotropic vapor-liquid equilibrium system of lighter compounds (lower boiling range) as it travels closer to the vapor-bitumen interface.

Similar phase equilibrium behaviours to pure components exists between the injected vapor and in-situ water in both HTMS-VAPEX (100% solvent) and AHTMS-VAPEX (azeotropic solvent-steam) processes. Figure 14 shows the reservoir properties map for HTMS-VAPEX and AHTMS-VAPEX process. As it is seen in the reservoir water saturation map, injection of 100% solvent in the HTMS-VAPEX results in in-situ water vaporization in the depleted chamber, moving the vaporized water and condensing it at semi-azeotropic condition on the vapor-bitumen interface. The temperature in the depleted chamber reduces from injection point to the interface (Note temperature map in Figure 14) as a result of preferential condensation of constituents of the multicomponent solvent and variation in water content in the vapor phase in vicinity of the vapor-bitumen interface. The temperature and water content of the vapor phase for HTMS-VAPEX are shown in Figure 15 for the location points depicted as points 1-7 in the temperature map shown in Figure 14. As it is seen in Figure 15, the temperature decreases from the injection temperature to the interface temperature. Also, the water content in the vapor phase exists only near the vapor-bitumen interface where the co-condensation of solvent compounds and steam occurs.

For the AHTMS-VAPEX in which diluent and steam are co-injected at semi-azeotropic condition, the in-situ water does not vaporize and remains in the liquid phase as is shown in water saturation map in Figure 14. The injected semi-azeotropic vapor temperature, changes due to preferential fractionation of the multicomponent solvent, however the temperature change from the injection point to the bitumen-vapor interface is not significant as it was seen for HTMS-VAPEX. The variation in the temperature and water mole fraction in the vapor phase for the points depicted in the temperature map of AHTMS-VAPEX in Figure 14 are shown in Figure 16. The vapor phase consistently contains a semi-azeotropic steam fraction (depending on the water-free local composition of the solvent compounds) and the temperature variation from injection point to vapor-bitumen interface is less than what is observed in HTMS-VAPEX case (Figure 15).

Similar improvements in key performance indicators of the AHTMS-VAPEX compared to HTMS-VAPEX is achieved with diluent-steam injection at semi-azeotropic condition. Figures 17, 18 and 19 show the bitumen recovery rate, enhancement effects in SolOR and PBRSR of AHTMS-VAPEX compared to HTMS-VAPEX process. As it is noted, the bitumen recovery rate is essentially the same in both processes. However, SolOR and PBRSR is improved significantly in AHTMS-VAPEX compared to HTMS-VAPEX due to semi-azeotropic solvent-steam injection.

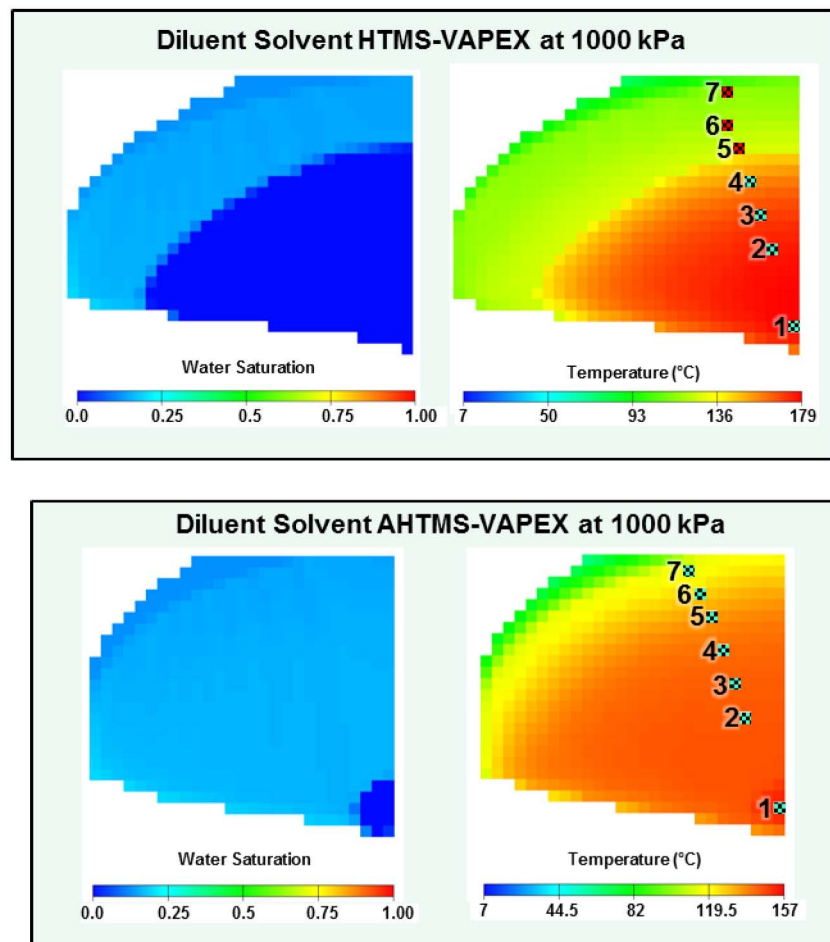


Figure 14—Comparison of reservoir properties map in HTMS-VAPEX and AHTMS-VAPEX Processes.

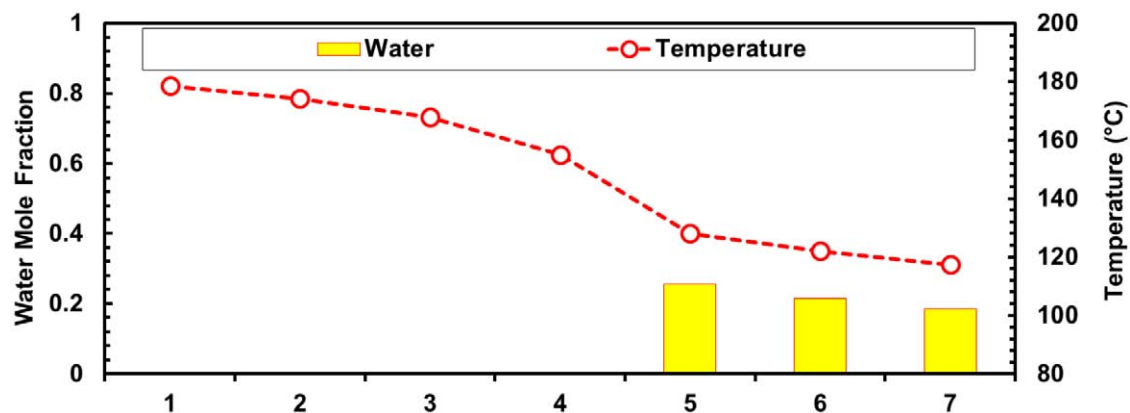


Figure 15—Depleted chamber temperature and water vapor model fraction variation in HTMS-VAPEX with diluent solvent (points correspond to Figure 14, HTMS-VAPEX case).

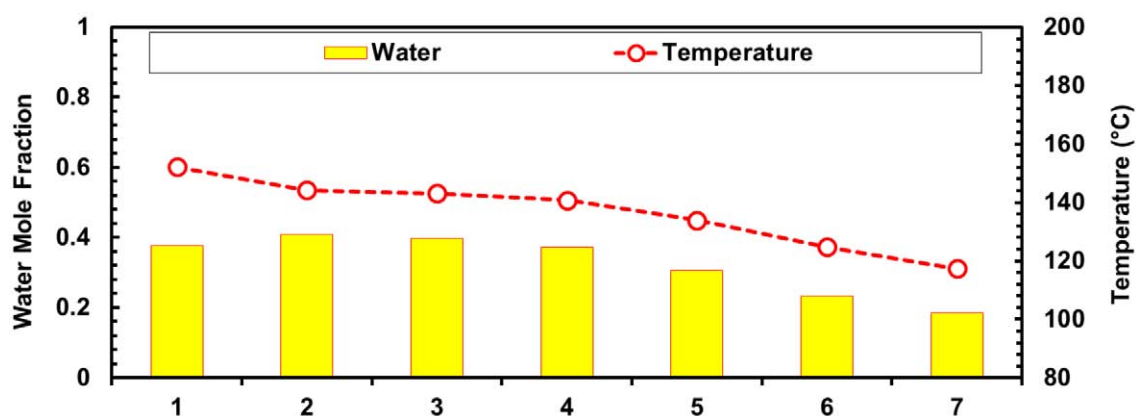


Figure 16—Depleted chamber temperature and water vapor model fraction variation in AHTMS-VAPEX with diluent solvent (points correspond to Figure 14, AHTMS-VAPEX case).

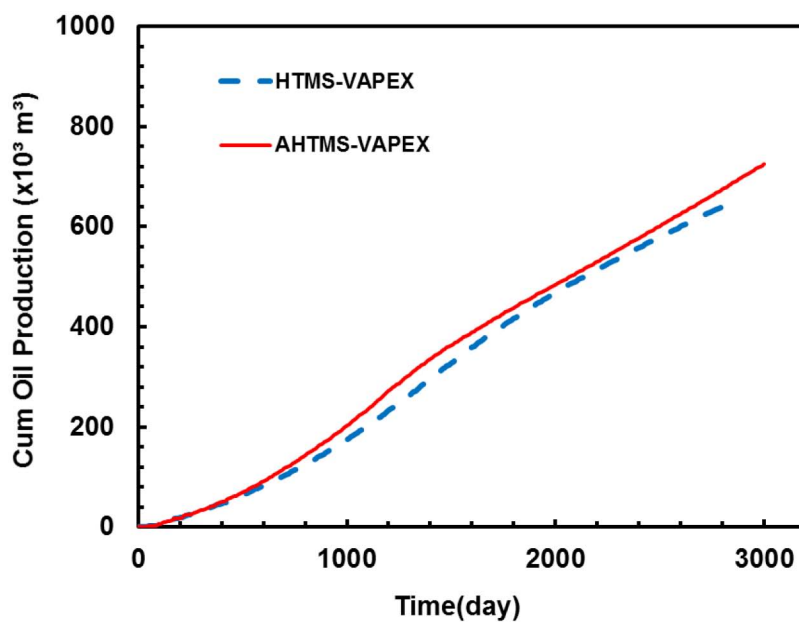


Figure 17—Comparison of cumulative bitumen production for HTMS-VAPEX and AHTMS-VAPEX with diluent solvent injection at 1MPa operating pressure.

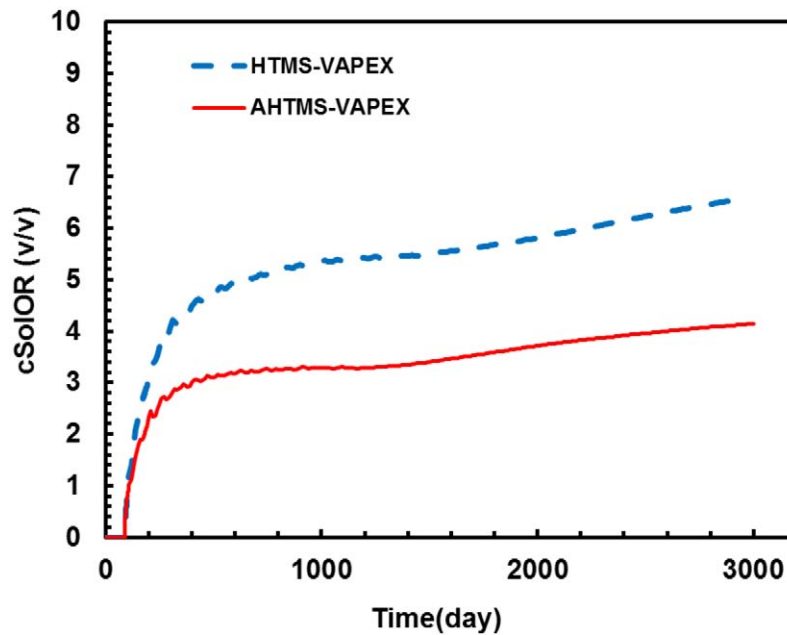


Figure 18—Comparison of cumulative SolOR for HTMS-VAPEX and AHTMS-VAPEX with diluent solvent injection at 1MPa operating pressure.

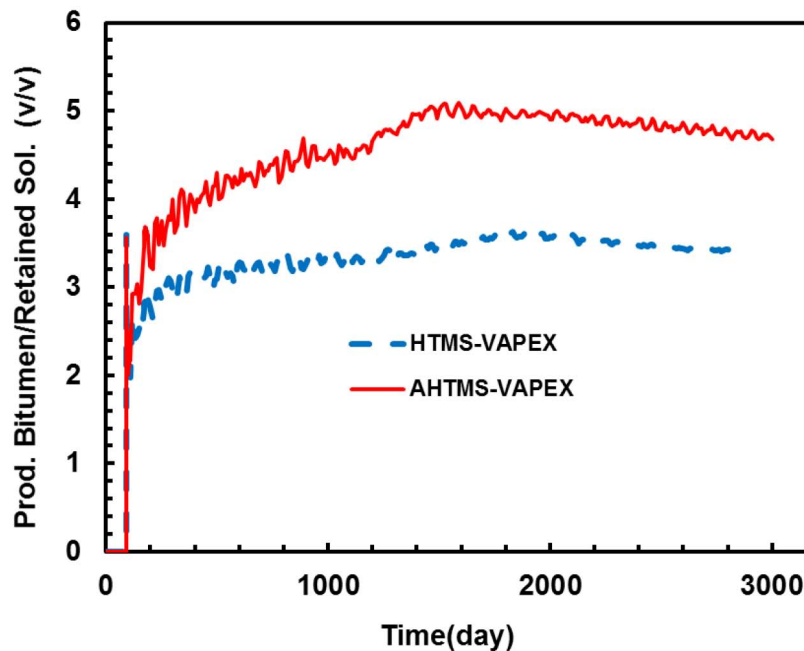


Figure 19—Comparison of produced bitumen-to-retained solvent ratio (BPRSR) for HTMS-VAPEX and AHTMS-VAPEX with diluent solvent injection at 1MPa operating pressure.

## Azeotropic Heated VAPEX Concept Validation and Performance Analysis-Laboratory Physical Modeling

An experimental laboratory program focused on a parametric study of the Heated VAPEX and Azeotropic Heated VAPEX processes is being conducted by Imperial-ExxonMobil. The experiments are conducted in a 1/100th scaled physical model utilizing fluids and model properties scaled to typical Athabasca oil sands reservoirs (Khaledi et al., 2012). The process performance is evaluated by conducting a series of tests under a wide range of operating conditions. The testing parameters include a range of operating pressures, solvent



types from light to heavy hydrocarbons, pure component vs. commercial multicomponent solvents (diluent), and Azeotropic Heated VAPEX vs. Heated-VAPEX.

The proof of concept of the developed Azeotropic Heated VAPEX recovery process and performance behaviors described in this papers have been validated in the laboratory. The detailed analysis of the experimental results is beyond the scope of this paper.

## Summary and Conclusions

A new thermal-solvent gravity drainage recovery process, known as Azeotropic Heated VAPEX, has been developed by Imperial-ExxonMobil. This process takes advantages of the azeotropic phase behavior of solvent-steam system to achieve the optimum performance of the recovery process. The thermodynamic properties including asphaltene/heavy liquid phase formation tendency of the hydrocarbon solvents when mixed with bitumen were analyzed and the selection of suitable solvents for Azeotropic Heated VAPEX process was discussed. The complex phase behavior of the solvent-steam systems is studied and the fundamental basis for a method of selecting the optimal fraction of steam and solvent is described. It was shown that the solvent-steam phase behavior in the Azeotropic Heated VAPEX recovery process is a complex phenomenon requiring detailed analysis for evaluating its impact on the process performance. This paper demonstrated that the injection of solvent-steam vapor mixture at azeotropic condition prevents in-situ water vaporization resulting in significant improvements in the process efficiency, reducing the solvent-to-oil ratio (SolOR) and the retained solvent in the depleted reservoir.

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