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Estimation Model for the Wax Crystal Size Distribution in Solvent Dewaxing Process

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Abstract: The wax crystallization in the solvent dewaxing is complicated process since it involves multi components flow with phase change of dissolved hydrocarbonates which solidified as wax crystals. In this study, an estimation mathematical model of the real solvent dewaxing unit was implemented. The model combined the energy balance equations and the mass-momentum balance in terms of the population balance for the kinetics of the wax crystallization phenomena. The transport equations were solved numerically to obtain the wax crystal size distribution, wax volume fraction along the pipeline of the heat exchanger and chiller in a solvent dewaxing process. Experimental measurements were conducted using Differential Scanning Calorimeter to analysis the dissolved temperature, onset crystallization temperature and the wax content. The results measurement results were used as the main input parameters to the model for the Crystal Size Distribution (CSD) prediction in Solvent Dewaxing. The developed numerical model was proved to be capable to predict wax crystallization characteristics for different operating conditions of such complex process.

Key words: Numerical model, solvent dewaxing, wax crystallization, crystal size distribution

INTRODUCTION

Solvent dewaxing is the most difficult and most important step for the base lube oil production. Wax is the most troublesome product in the manufacture of lubricating oil. Its presence in lubricating oils prevents free movement at lower temperatures (Sequerira, 1994). One of the separation technique of the wax components is done by solvent dewaxing which selectively removes higher carbon number n-paraffins due to the highest crystallization temperature where the dewaxed oil dominated by non normal paraffins and contains also lower carbon number of normal paraffins (Thomas, 2008). The waxy lube oil-solvent mixture was chilled at a specified cooling rate in a series of hairpin double pipe Scraped Surface Heat Exchangers (SSHE) and chillers. This method is one of the most popular for dewaxing oils and deoiling waxes because it allows variation in the dilution ratio of the feedstock with solvent in optimum range without affecting the cooling rate and degree of supersaturated concentrations of the flow. Solvent dewaxing is a chemical separation process in which no chemical reactions occur. The composition of the dewaxed oil is completely dependent on the waxy feed and it represents the subtraction of the wax composition. An experimental study was conducted to compare the normal paraffin distribution between solvent and catalytic lube oil dewaxing by analyzing the feedstocks and products from

processes (Taylor and McCormack, 1992). The chemical analysis of the carbon number distribution for three paraffinic wax samples were conducted using high temperature Gas Chromatography (GC) methods. The results showed that the distribution of normal and non-normal hydrocarbons remaining in the oils after dewaxing process was clearly different and this suggested that the two processes have different ways in removing the higher paraffin. There are limited literatures dealing with crystallization process in the SSHE, These studies introduced a numerical simulation of the fluid flow and heat transfer combined with the population balance to represent the kinetics of ice particles crystallization using commercial CFD software such the works that conducted by Lian *et al.* (2006) and Benkhelifa *et al.* (2008).

The publication of the modeling analysis in the dewaxing lube oil feedstock in SSHE for the previous studies was found to be very limited. Bessarabov *et al.* (1996) proposed an analytical model (1-D) transient of the dewaxing process from a raffinate-solvent solution, the authors suggested that the temperature distribution of accumulated wax layer on pipe wall between two adjacent rotational scrape blades actions can be solved combined with wax crystallization kinetics. The kinetics of crystallization processes is described by using jth moment transformation of population density function. A suggestion that the wax crystallized on the inside tube wall in scraped channel has the form of a hollow cylinder

layer, so in order to solve the kinetic problem of wax crystallization in such a way that the temperature distribution in a wax layer crystallized on the tube wall at any moment of time must be determined. Li *et al.* (2008) conducted a one dimensional parallel flow direction in steady state condition. The authors used a pilot plant for his model, consists of four single elements of SSHEs with multi solvent dilution points after each exchanger. The operation condition including the temperature distributions, solvent composition, wax compound and the crystallizer dimensions were examined. The results discussed the effect of operational condition on the wax crystal size distribution in the wax-oil-solvent solution. The previous literatures suffer a lack of the studies that deals with the analysis of the combination between the heat exchangers rating mode and wax crystallization kinetics of real solvent dewaxing in the SSHEs and chillers. The reason behind this that those processes are confidential to the petroleum industry companies beside that the design data for the plant depended on the physical properties that predicted experimentally for each lube oils feedstock. The major objective of this study is to develop a general numerical model to characterize the wax crystallization process for waxy paraffin oils in double pipe SSHEs and chillers in a typical MEK dewaxing unit. This model consists of combination of the kinetics of wax crystallization with heat transfer.

Mokhlif and Al-Kayiem (2011) presented analytical model and analysis for the periodic deposition and removal of the wax in a solvent dewaxing process in a lubricating oil manufacturing.

The main aim of the present study is to present a mathematical procedure to predict the wax crystallization in the solvent dewaxing process. The procedure involves experimental and numerical analysis. The experimental part consists of measuring the dissolved temperature, onset crystallization temperature and the wax content. The Differential Scanning Calorimeter (DSC) has been used as the main equipment for the thermal properties measurement and analysis.

MATHEMATICAL MODEL

Heat transfer model: The SSHE’s performed as a counter current system, hence, in order to simulate the double pipe SSHEs numerically; the model equations for heat transfer balance for a segment for both fluids in steady state condition are as follows:

$$m_h C_{ph} \frac{dT_h}{dz} = -UP(T_h - T_c) \tag{1}$$

where m_h , C_{ph} , T_h and T_c are the hot fluid mass flow rate, heat capacity, hot fluid temperature and cold fluid temperature, respectively.

The differential equation for the cold fluid (filtrate) side is as follows:

$$m_c C_{pc} \frac{dT_c}{dz} = UP(T_h - T_c) \tag{2}$$

where, m_c , C_{pc} are the cold fluid mass flow rate and heat capacity, respectively.

The equations above can be solved with the boundary conditions as follows:

$$\text{At } z = 0 \quad T_h = T_{hi}$$

$$\text{At } z = L \quad T_c = T_{ci}$$

The two ordinary differential equations above are of the kind of two boundary value problems and can be solved using Runge-Kutta combined with the shooting method (root finding) (Muralidhar and Sundararajan, 2003). Solving Eq. 1 and 2 depending on using the suitable empirical correlations for heat transfer coefficients in both sides of the heat exchanger beside the available methods to identified the physical properties of the fluids. The overall heat transfer coefficient U in the equations mention above can be calculated based on the outer surface of the heat exchange tube as follow:

$$U_o = \frac{1}{\frac{D_o}{D_i} \frac{1}{h_i} + \frac{D_o \ln D_o / D_i}{2k} + \frac{1}{h_o} + h_f} \tag{3}$$

where, h_i and h_o are the heat transfer coefficients for inner pipe (scraper channel) and the outer tube, respectively. The fouling factor h_f represent the deposit thermal resistance just for the outer pipe where inside pipe is clean surface due to scraping effect.

The heat transfer coefficient h_i can be predicted using the correlation below for crystallization process (Lakhdar *et al.*, 2005):

$$Nu = 0.63 Re_r^{0.61} w_{w0}^{0.34} \tag{4}$$

where, Re_r is the rotational Reynolds number and w_0 is global mass fraction.

For forced convection in turbulent flow where Reynolds number >2300 we can use Gnielinski correlation as follow (Incropera, 2007):

$$Nu_{tube} = \frac{f/8(Re-1000)Pr}{1+12.7(f/8)^{0.5}(Pr^{2/3}-1)} \left[1 + \left(\frac{D_h}{l} \right)^{2/3} \right] \times \left(\frac{Pr}{Pr_w} \right)^{0.11} \tag{5}$$

where, f is the Darcy friction factor that can either be obtained from the Moody chart or for smooth tubes from correlation developed by Incropera (2007):

$$f = (1.82 \cdot \log \text{Re}) - 1.64)^{-2} \quad (6)$$

The Gnielinski Correlation is valid for:

$$(0.5 \leq \text{Pr} \leq 2000) \text{ and } (3000 \leq \text{Re} \leq 5 \times 10^6)$$

The corrected Nussle number for the concentric annular ducts with heat transfer at the inner wall and the outer wall is insulated we can use the Petukhov and Roizen correlation as follows (Incropera, 2007):

$$\text{Nu} = \text{Nu}_{\text{tube}} \cdot 0.86 (D_o/D_i)^{0.16} \quad (7)$$

In the evaluation of the overall heat transfer coefficient, the surrounding temperature, i.e., the chiller temperature is assumed constant along the pipe, where the fluid in the annulus is working as a flooded refrigerant system.

Kinetics of wax crystallization: Particles conservation in any system is governed by the particle number continuity equation, essentially a Population Balance (PB) to identify particle numbers in each and every size range and account for any changes due to particle formation. The PB equation of nucleation and crystal growth is expressed as follows:

$$V \frac{\partial n}{\partial z} + \frac{\partial(nG)}{\partial L} = B \delta(L - L_c) \quad (8)$$

where, $n = dN/dL$ is the crystal population density, (number of crystal per unit size per unit volume of system), $G = dL/dt$ is the crystal growth rate and $B = dN/dt$ is the nucleation rate, V is the mean velocity and δ is the Dirac function meaning that nucleation creates crystals with a size equal to critical size L_c .

Most recent studies employed ‘moment method’ to solve the PB. The j th moment M_j of the population density function is defined as (Mullin, 2001):

$$M_j = \int_0^\infty L^j n(L, z) dL \quad (9)$$

The moment equation above can be rearranged for steady flow as follows:

$$V \frac{dM_j}{dz} = jGM_{j-1} + BL_c^j, \quad j = 0, 1, 2, 3 \quad (10)$$

The first four moments represent the total crystal number, total crystal length, total surface area and crystal mass (phase volume of the dispersed particles).

The initial boundary conditions to solve Eq. 15 depend on assumption that the number of crystals at the inlet of the heat exchangers is zero.

The overall nucleation rate can be predicted from the empirical form Mullin (2001):

$$B = k_b \Delta C^b \quad (11)$$

where, k_b is the nucleation constant, b is the nucleation reaction order and ΔC is the difference in concentration (supersaturation).

The growth rate may be expressed as Mullin (2001):

$$G = k_g \Delta C_g \quad (12)$$

where, k_g and g are the crystal growth constant and index, respectively.

In crystallization work the exponent g which applied to a concentration difference, has no fundamental significance and cannot give any indication of the number of elementary species involved in the growth process. Depends on this assumption the first order ($g = 1$) will take in this study.

To calculate ΔC , the solubility for the wax dissolved in oil-solvent solution is required. The n-paraffins in wax content extended from C_{19} or C_{20} to C_{40} or even C_{53} (Dirand *et al.*, 1998) and this depended on the chemical analysis of the feedstock to predict the n-alkanes distribution in wax content.

As the solubility of such multi-component solution is much complex, in such a case the wax (solute) and the oil portion can be treated as single component. This treatment is much dependent on two major parameters, (i) the mass fraction of the wax in the lube oil feedstock and (ii) the dissolved temperature of this wax and this can be proved from the chemical analysis of the feedstock.

The correlation model for the solubility of n-alkanes dissolved in organic solvents is as follows by Haulait-Pirson *et al.* (1987):

$$\begin{aligned} \ln \phi_{w,i} = & -\frac{\Delta H_m}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) - \frac{\Delta H_1}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \\ & + 0.5 \ln \left[\phi_{w,i} + (1 - \phi_{w,i}) \frac{\bar{V}_w}{\bar{V}_i} \right] - 0.5 (1 - \phi_{w,i}) \left(1 - \frac{\bar{V}_w}{\bar{V}_i} \right) \\ & - \frac{(1 - \phi_{w,i})^2 \bar{V}}{RT} (\delta_w - \delta_i)^2 \end{aligned} \quad (13)$$

where, the subscript, i represent the solvent portion which refer to Toluene, Methyl Ethyl Ketone (MEK) and the liquid oil in the solution. The mass fraction of the wax w_{wi} can be predicted with the equation (Haulait-Pirson *et al.*, 1987):

$$\phi_{w,i} = \frac{w_{w,i} \bar{V}_w M_i}{w_{w,i} \bar{V}_w M_i + (1 - w_{w,i}) \bar{V}_i M_w} \quad (14)$$

Equation 13 and 14 are solved numerically by Root Finding iteration method.

In order to calculate the particle size distribution, the log-normal function is adopted by Li *et al.* (2008):

$$n(L) = \frac{m0}{\sqrt{2\pi}L\beta} \exp\left(-\frac{(\ln L - \ln L_\epsilon)^2}{2\beta^2}\right) \quad (15)$$

where, L_ϵ and β are the geometrical standard size and standard variance of the distribution and the formulated description for there are as follow by Li *et al.* (2008):

$$\beta^2 = \ln\left(\frac{m2.m0}{m1^2}\right) \quad (16)$$

$$L_\epsilon = \frac{m1}{m0.exp\left(\frac{\beta^2}{2}\right)} \quad (17)$$

To accomplish the mathematical model many data are required, including the dimensions of exchangers, operation condition, physical properties of oil and wax, kinetics constants of the wax components and carbon distribution of n-paraffins in each feedstock. The model is written in MATLAB computer language.

EXPERIMENTAL MEASUREMENT

All the experiments were performed on SN150 lube oil feedstock obtained from distillation of Kirkuk crude in Baiji Refinery, Iraq. The lube oils feedstock charged to the dewaxing unit were treated in a deasphalting process to remove the asphalt and resin while the solvent extraction unit was used to reduce the aromatics components. The following experiments were carried out:

Differential scanning calorimetry test: Differential Scanning Calorimetry DSC is a method used to analyze the melting and crystallization regions of materials. It is capable of evaluating a great amount of data which are collected simultaneously with quality and stability. The major parameters which can be predicated from the thermal analysis of the DSC are the onset crystallization temperature, dissolution temperature and the wax content (Chen *et al.*, 2004).

The thermal analyses were performed using Pyris 1DSC apparatus consisted of a measurement unit for setting and measuring the sample and a base unit for

processing signals sent from the measurement unit. The acquired data are sent to the data acquisition software for analysis. The two measurement chambers of the DSC are designed to measure the heat flux. To predict the wax content by using the thermal analysis of the DSC scan. The procedure is developed by Chen *et al.* (2004) which depended on computing the total thermal heat released of wax crystallization. This can be done by integrating the area under the deflection curve between the onset and endset intersection temperatures points of base line.

An empirical formula is suggested by Chen *et al.* (2004), connecting the heat released and the wax content also allows the prediction of the wax content from the measure of the total heat (Q_{oil}/Q_{wax}) as follows:

$$w_w = 0.75Q + 0.2 \quad (18)$$

For Acetone method the empirical equation is:

$$w_w = 0.73Q + 0.74 \quad (19)$$

where, w_w (wt. %) wax content and Q is the total heat in (J/g).

RESULTS AND DISCUSSION

The predicted wax content from the DSC thermal analysis of the sample using the empirical correlations are illustrated in Table 1.

Figure 1 and 2 illustrate the DSC thermal analysis of the SN150 feed sample mention above, before and after dewaxing process, respectively.

Figure 3 illustrates the comparison of wax content of the SN150 lube oil feedstock with the predicted solubility of the closest higher carbon number of the n-paraffin that represent the solid wax dissolved in Decane n-C₁₀ or Undecane n-C₁₁ as light liquid portion of the feed solution.

The feedstock pumped to the SSHEs at initial temperature of 322 K for the sample SN150 above each desired cloud point. The kinetics constants of the wax crystallization, in special case the crystal growth constant (k_g) which is difficult to find publishing works of the n-alkanes that extended from n-C₂₂ to n-C₃₂ in this study. However, the fitting of the k_g can be predicted from the wax mass fraction removal which depended on the

Table 1: Predicted wax content of lube oils samples

Samples	Q_{oil}/Q_{wax} method (wt.%)	Acetone method (wt.%)
Feedstock SN150	0.2860	0.2838
Base SN150	0.1255	0.1276
Recovery SN150	0.1605	0.1562

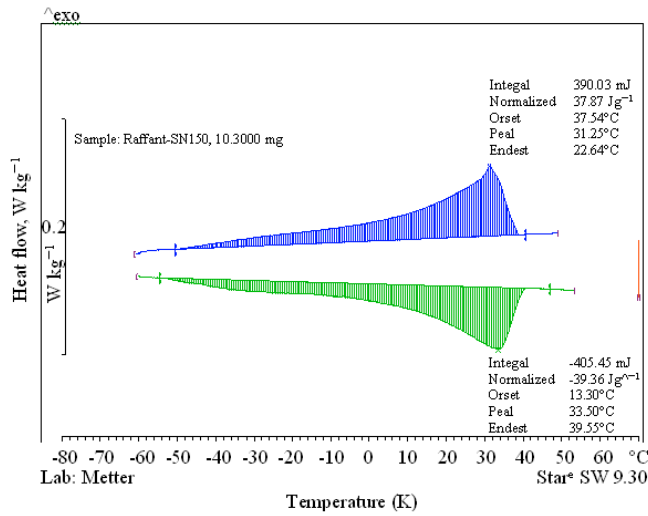


Fig. 1: DSC thermal analysis for Feedstock SN150 before dewaxing

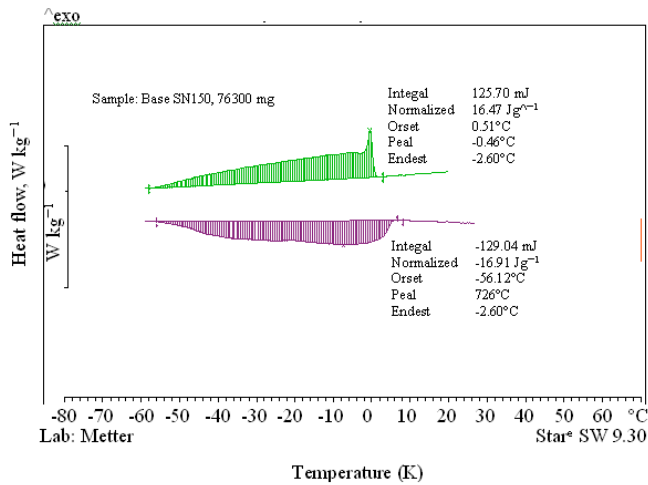


Fig. 2: DSC thermal analysis for Base SN150 after dewaxing

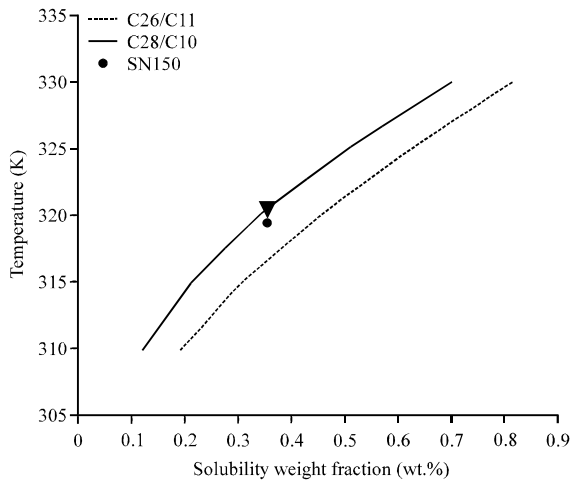


Fig. 3: Solubility model for C_{26} in C_{11} and C_{28} in C_{10} compare with mass fraction of SN150 feedstock

experimental thermal analysis of DSC tests of the feed before and after dewaxing. The predicted moments from the model will give the characteristics for the wax crystals in exit of the pipe before filtration. The mass yield of the wax or the removable solid can be predicted from the third moment, in order to support the nucleation constant with available experiments. Figure 4 illustrate the predicted wax mass fraction along the pipe line after prediction the moment which represents the solid fraction and the assumption of spherical shape of the crystal the volume and the mass fraction can be predicted. The distribution along the pipeline shows rapid increased after onset crystallization due to releasing of heat of fusion of nuclei particles and mention that this region demonstrated by nucleation process.

The Crystal Size Distribution (CSD) of the wax crystallization at the exit of the heat exchangers is shown in Fig. 5.

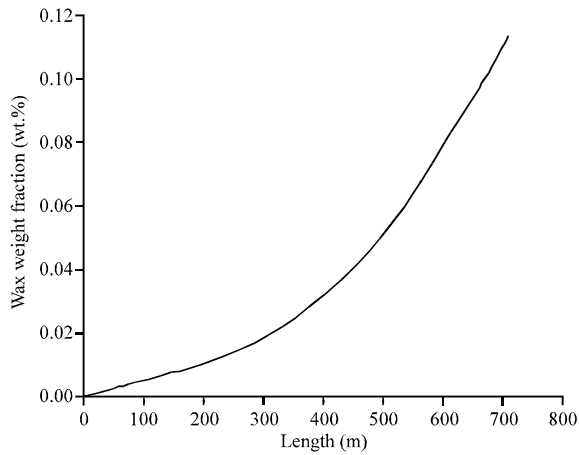


Fig. 4: Solid mass fraction distribution along SSHEs and chillers

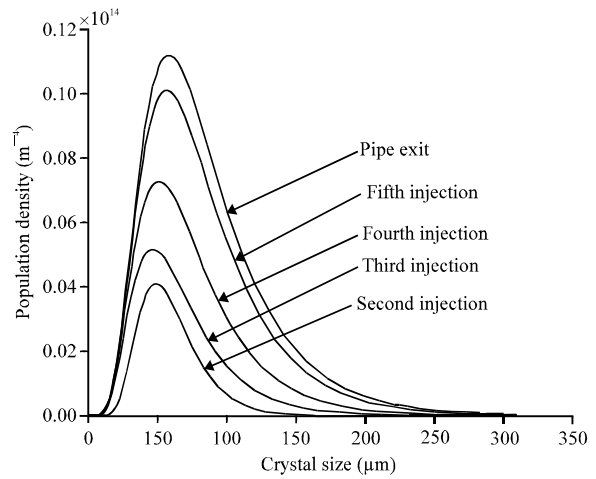


Fig. 6: Predicted crystal size distribution at different solvent injection point

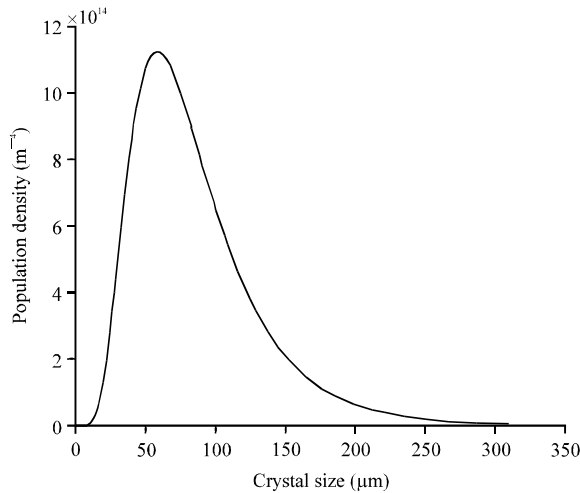


Fig. 5: Predicted crystal size distribution of the removed wax at the exit

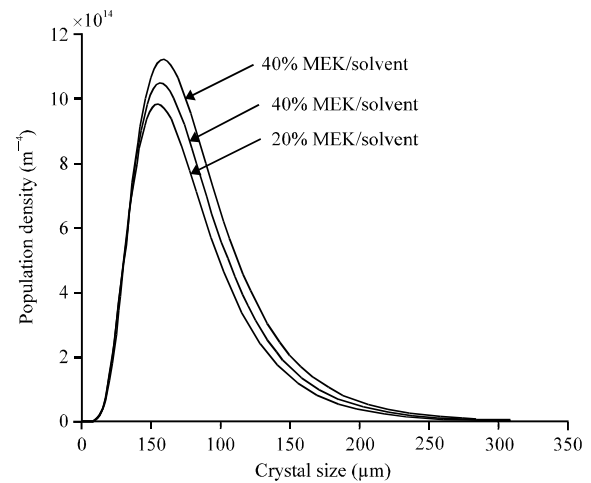


Fig. 7: Predicted crystal size distribution at different MEK percentage ratio

The results taken into account the liquid portion of the oil in the mixture represented by C10 and C11 which shows no big difference between the two components. Study of the effect of the operation conditions on the CSD are illustrated in Fig. 6 and 7, respectively. In Fig. 6 shows the wax CSD after each position of the solvent injection points. The injection point for solvent should not effect on the linearity of the wax crystallization in the suspension system and this need controlling of the temperature of the solvent injected in the solution.

Figure 7 shows the effect of the ratio of the MEK in solvent mixture where the high content of

MEK in solvent dewaxing process is beneficial to produce a large number of the crystal with large sizes.

CONCLUSION

The developed model specifies the crystals characteristic in the SSHEs and chillers in solvent dewaxing unit. The n-alkanes solubility model give a suitable choice for the carbon number existed in the solid wax which attaches the wax weight fraction and dissolving temperature of the feedstock, this assumption allowed to represent the physical properties of the wax-oil-solvent mixture in both the dissolution region and the crystallization region. Knowing the global wax mass

fraction and the dissolved temperature of the feedstock are very important parameters to handle with crystallization kinetics of the solution system. The flow behavior is much dependent on the controlling of the solvent ratio in order to keep the flow diluted and suspension. The predicted simulation results implemented on real operation data collected from the field. The predicted wax crystal size distribution at exit of the chillers was fitted with removal wax that predicted from the DSC thermal analysis. The established model can be applied for different arrangement and different feedstock for solvent dewaxing, but it is important to have the system exact compositions for all the processing material.

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