CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci

Copyright © 2009, AIDIC Servizi S.r.l., ISBN 978-88-95608-01-3 ISSN 1974-9791
DOI: 10.3303/CET0917299

Determination of a physical-chemical parameter for modelagem process of molecular distillation

Julie Andrea Ballesteros Hernández[1], Lamia Zúñiga Liñan[1], André Jardini[1], Ma. Regina Wolf Maciel[1], Rubens Maciel Filho[1], Lilian Carmen Medina[2].
1. State University of Campinas. 2. PETROBRAS
Av. Albert Einstein, 500. CEP 13083-852. Campinas, SP, Brasil.

The mathematical modeling and simulation of the process of molecular distillation of descending film has been presented as a powerful tool for predicting the response of variables in the purification of pharmaceutical products sensitive to heat such as vitamins and related compounds, the fine chemicals (Batistella and Wolf Maciel, 1996 and 1999). However, there are still no work of modeling and simulation that address the characterization of heavy oil fractions nationals.
In the development of the specific mathematical modeling for heavy and ultra heavy petroleum fractions in a molecular distiller is very important the definition of physical and chemical parameters as density and specific heat of the mixture, the enthalpy of vaporization, among others, since they are used in the energy balance. Information on these properties and their variation with temperature are found in the open literature for mixture with few components (simple mixtures). However, for multicomponent solutions consisting of complex mixtures such as oil and its heavy and ultra-heavy fractions, available data are few, or are limited to low temperatures. The specific heat is an important property in the energy balance. This property can be measured by Differential Scanning Calorimetry (DSC), which gives results with great sensitivity and accuracy.
This paper presents the variation of specific heat with the temperature of ultra-heavy oil fractions in the range from 80° to 350 ° C . Through the study of this variation, the equation nowadays used can be adjusted, in order to determine the specific heat. New values of the constants are determined, so that the equation can be used for these complex products, optimizing the estimative of Cp and so no experimental data are always necessary for simulations.
Within this context, the modeling will be adjusted and the results of the simulation will be validated with experimental data.

1. Introduction

The process of molecular distillation gives fractions of waste oil in the range of 500 ° C to 700 ° C, thereby allowing the expansion comes the characterization of oil, largely from extraoil. For the definition of operating conditions and optimization is necessary to the development of mathematical modeling this process, and this model is of great

Please cite this article as: Ballesteros Hernandez J.A., Zuniga Linan L., Jardini A., Wolf Maciel M.R., Maciel Filho R. and Medina L.C., (2009), Determination of a physical-chemical parameter for modelagem process of molecular distillation, Chemical Engineering Transactions, 17, 1789-1794 DOI: 10.3303/CET0917299

importance to development of physical- chemical properties as density, viscosity, thermal conductivity and specific heat, the products involved in process, because these properties are applied directly on balances of mass and energy, or are used as intermediaries in the calculation of parameters such as: the heat capacity which is determined by the specific heat.

Data these properties depending on the temperature at which the material is subjected are found in the literature for solutions of a few components. However, for multi-component solutions and complex mixtures such as oil, heavy cuts and waste data are few. Besides its use in modeling the molecular distiller, the heat capacity is obligatory in the processes of refining oil as the atmospheric distillation, distillation vacuum and cracking (Zanier e Jackle, 1996)., because it is a basic parameter for the solution of energy balance equations.

As an extensive property of the thermodynamic point of view, the heat capacity (C) is obtained by the specific heat (Cp) of the sample and its mass. The determination of this property experimentally allows adjustment of the parameters of existing models to calculate the variation of heat capacity with temperature for the heavy fractions studied. It is may be determined by the technique of Differential Scanning Calorimetry (DSC), with great sensitivity and precision.

The technique of Differential Scanning Calorimetry (DSC) recorded on a continuous basis the apparent heat capacity or specific heat of any macromolecule according to temperature, through a thermograms. This is characterized by a peak of heat absorption corresponding to a transition process or thermally induced, which, according to the second principle of thermodynamics (considering the case in equilibrium), is a procedure endothermy.

The DSC can also provide global parameters, such as changes in enthalpy [ΔH] of entropy [ΔS] of Gibbs free energy of [ΔG] associated with the transition induced by temperature.

In this study, experiments were conducted to determine the specific heat of cuts and waste from two Brazilian oil obtained from the molecular distillation process, in order to adjust the values of A and B of the equation that determines the specific heat for this type of sample, Enabling a better estimate these, and their mathematical application in energy balance.

2. Methodology and Equipment

Oil with ºAPI less than or equal to 25 were obtained by atmospheric and vacuum distillation (100 and 2 mmHg) according to ASTM D2892, resulting in the residue 400 ° C +, which was the charge of the process of molecular distillation. The molecular distillation generates cuts and waste in the range of temperature of 500 ° C to 700 ° C, which were analyzed using the Differential Scanning Calorimeter, DSC 823e (belonging to the LOPCA / FEQ / UNICAMP), in the range of temperature from 80 to 350 ° C. This range of temperatures corresponds to the operating temperatures of molecular distiller, for which we are doing the modeling and simulation, and the limit is also intended to prevent the degradation of oil.

Before conducting the experiments, the equipment was calibrated with a standard method for automatic evaluation and verification of results confirms (indium check), which is based on measurements of the melting point and heat melt of the chemical element indium (In). We used a heating rate of 10.0 ° C / min., a range temperature of 120,0-180,0 ° C and a mass of the element indium (In) of 6.3 mg.
Each sample was weighed on a digital scale directly in the crucibles used in the equipment and they were sealed by means of a press. The lid of each crucible was punctured to allow the release of fumes or gases obtained by heating the samples. These samples are placed in a compartment of the equipment that has another empty crucible, which was used as a reference in measuring the calorific capacity.

2.1 Test Exploration
With exploratory purposes, was an initial test, considering a wide range of temperature of 25 ° C to 600 ° C oil Gamma (fantasy name), with the experimental conditions written in Ribeiro *et al.* (2004). A flow of gas purge of 50 mL / min, a heating rate of 10 ° C / min and nitrogen as a purge gas was used.

2.2 Applied Methodology
Considering the results of exploratory test was set the temperature range of 80 ° C - 350 ° C for the test, maintaining the same flow of gas purge of 50 mL / min nitrogen and heating rate of 10 ° C / min .
To calculate the heat capacity of samples, the equipment uses the dynamic equation of the definition of specific heat as follows:

$$C_p = \frac{dH}{dt} \cdot \frac{dt}{dT_s} \cdot \frac{1}{m} \quad (1)$$

$\frac{dH}{dt}$: Flow of heat to the sample.
$\frac{dt}{dT_s}$: Current warming rate of the sample.
m : Mass of the sample.

3. Results

The process of molecular distillation gives fractions of waste oil in the range of 500 ° C to 700 ° C, thereby allowing the expansion comes the characterization of oil, largely from extraoil. For the definition of operating conditions and optimization is necessary to the development of mathematical modeling this process, and this model is of great importance to development of physical- chemical properties as density, viscosity, thermal conductivity and specific heat, the products involved in process, because these properties are applied directly on balances of mass and energy, or are used as intermediaries in the calculation of parameters such as: the heat capacity which is determined by the specific heat.

3.1 Test Exploration
The test described in section 2.1 were obtained profiles of variation of heat flux and specific heat with temperature, for oil Gamma. In this test was noted that from 400 ° C,

the curve of specific heat shows irregularities that show the beginning of thermal decomposition of the sample (thermal cracking). For this reason, the range of temperature for the following analysis was reduced to the range of 80 to 350 ° C and also because this range of temperature corresponds to the operating temperatures of molecular distiller, for which we are doing the modeling and simulation.

3.2 Applied Methodology

In Figures 1, 2 and 3 are presented, respectively, the profiles of variation of specific heat with temperature for:

- Cuts 400 - 537°C, 400 - 554°C, 400 - 584°C, 400 - 620 °C e 400 – 670 °C of Zeta Oil,
- Cuts 400 - 537°C, 400 - 554°C, 400 - 584°C, 400 - 620 °C e 400 – 670 °C of Gamma Oil,
- Waste, 537 °C+, 554 °C+, 583 °C+, 620 °C+ e, 670,00°C+. of Gamma Oil, all obtained by molecular distillation.

It is a linear growth of specific heat with the temperature of the test until the value of 250 ° C, for all the samples analyzed from cuts, and up to 300 ° C for all samples of waste.

For the oil Zeta, is to arrange the slices in accordance with its Cp, we obtain the sequence:

Cp (400 – 537 °C) > Cp (400 - 554°C) > Cp (400 - 670°C) > Cp (400 - 620°C) > Cp (400 - 583 °C).

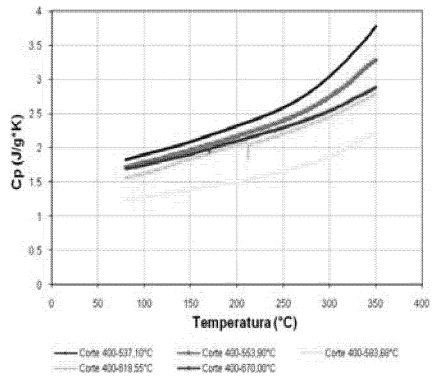

Figure 1 – Specific Heat vs. Temperature of the experiment for Cuts Oil Zeta.

It appears that as the cuts are lighter, present a final temperature of boiling lower, its specific heat Cp increases, except for sections 400 - 620 ° C, 620 - 670 ° C, which does not fall into this initial analysis.

For Gamma oil, you can see that the specific heat of samples of cuts increases as are heavier, that is, with increasing temperature the final cut, except for cutting 400 - 583. Explaining to the cuts in oil Gamma: Cp (400 – 670 °C) > Cp (400 - 620°C) > Cp (400 - 554°C) > Cp (400 - 537°C) > Cp (400 - 583 °C),

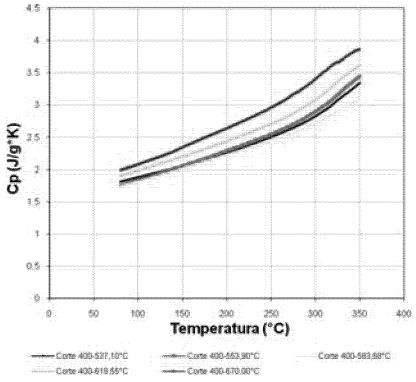

Figure 2 – Specific Heat vs. Temperature of the experiment for Cuts Oil Gamma.

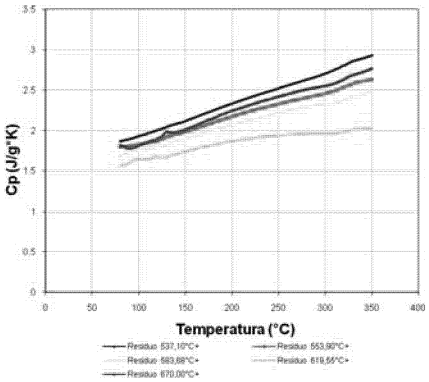

Figure 3 – Specific heat vs. Temperature Experiment for the Gamma Waste Oil

The profiles of specific heats Cp waste oil Gamma indicate that the waste obtained at higher temperatures have the lowest values of Cp, explaining, for waste oil Gamma: Cp (537 ºC+) > Cp (670º C+) > Cp (554 ºC+) > Cp (583º C+) > Cp (620ºC+).

This behavior can be explained by the potential of molecular distiller to separate the lighter components in the stream of distillate and the heaviest components in the stream of waste.

For the development of mathematical modeling of molecular distiller is necessary to have a relationship between the distillation temperature and specific heat. To calculate the specific heat Cp, applies the equation below (Perry & Chilton, 1999):

$$C_p\left[cal/(g.°C\right] = A/\sqrt{d_4^{15}} + B\left(t-15\right) \qquad (2)$$

where $d_4^{15} \rightarrow$ Density on the reference temperature of 15.5 ° C.

$t \rightarrow$ Temperature, °C

that needs to be readjusted to the cuts and waste of heavy oil, through the determination of new specific values for the constants A and B in each range of temperature studied. That determination was made by values of specific heat obtained experimentally for the cuts made at temperatures known. The constants obtained are presented below in Tables 1 and 2:

Table 2 Constants A and B for calculating the Cp of Zeta oil.

Cuts (°C)	*A (cal/(g.°C))*	*B (cal/(g.°C^2))*
400-537,10	0,34162	0,00116
400-553,90	0,32949	0,00101
400-583,68	0,25018	0,00061
400-619,55	0,30815	0,00091
400-670,00	0,34211	0,00085

Table 1 Constants A and B for calculating the Cp of Gamma oil.

	A (cal/(g.°C))	*B* (cal/(g.°C2))		*A* (cal/(g.°C))	*B* (cal/(g.°C2))
Residue 400 °C+	0,32389	0,00091			
Cuts (°C)			**Residue (°C)**		
400-537,10	0,35319	0,00101	537,10	0,38759	0,00091
400-553,90	0,33219	0,00115	553,90	0,37829	0,00075
400-583,68	0,34029	0,00101	583,68	0,36689	0,00069
400-619,55	0,36578	0,00118	619,55	0,36100	0,00044
400-670,00	0,37002	0,00142	670,00	0,38415	0,00083

4. Conclusions

Through the method of differential scanning calorimetry profiles were obtained from the variation of specific heat as a function of temperature for samples of cuts from the distillation (ASTM D-2892) and fractions of distillate and residue from the process of molecular distillation. There was an increase in the specific heat with the temperature of the experiment for all samples.

In general can say that the extent to which the track distillation of the product increases, also increases the specific heat, but it has a strong influence of the density of each sample which can lead to contradict this statement, In addition to the samples are obtained by a very new methodology, molecular distillation, but can not reach definitive conclusions.

In particular for heavy waste, there was a decrease of specific heat with the temperature increase of molecular distillation. This behavior must be explained by the presence of components aromatic type and asphalt type of high molecular weight in these currents, which would impede the rapid thermal variation of these samples to receive a certain amount of heat, but it needs to also be better investigated.

The differential scanning calorimetry allows the experimental determination of specific heat of heavy oil fractions, allowing to adjust values of A and B presented the equation, which is of importance to the development of equations of energy balance in mathematical modeling of the molecular distillation, as this model is implemented based on specific heat

References

Perry, R.H. Perry´s Chemical Engineers´ Handbook, 7 ed., p. 186, 1999.

Ribeiro, D.A.; Gonçalves, M.L.A.; Teixeira, A.M.R.; Pinto da Mota, D.A.P; Gomes Texeira, M.A. Estudos por análise térmica da influência dos asfaltenos no craqueamento de resíduo de destilação atmosférica de petróleos brasileros. 3° Congresso Brasileiro de P&D em Petróleo e Gás. Salvador, 2004.

Winter A., Sbaite P., Batistella C. B., Maciel Filho R., Wolf Maciel M. R., Medina L., Gomes A., Kunert R., Mathias Leite L. F. e Pontes Bittencourt C. Caracterização de correntes de resíduos pesados de petróleos obtidas pelo processo de destilação molecular. Anais do 3° Congresso Brasileiro de P&D em Petróleo e Gás, 2005.

Zanier, A.; Jackle, H.W. Heat capacity measurements of pretroleum fuels by modulated DSC. Thermochim. Acta, v.287, p. 203-212, 1996.