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EFFECT OF THE NUMBER OF N-ALKANES CONSIDERED IN GASOLINE MODELLING TO ESTIMATE NUCLEATE BOILING HEAT TRANSFER COEFFICIENT

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Abstract. *Because gasoline is a mixture of hundreds of components, estimating its properties or phase equilibrium parameters is virtually impossible and, by consequence, calculating its heat transfer coefficient in nucleate boiling is not feasible by using available correlations in the literature. One common technique for making possible the calculations with complex mixtures such as oil products and fuels is to replace them by surrogates, which are simpler mixtures that emulate the desired characteristics of the complex target-fuel. Considering only the n-alkanes group to model nucleate boiling with gasoline, the present work analyzes the effect of varying the number of components considered in surrogates. Furthermore, the results for the heat transfer coefficient obtained with well-established nucleate boiling correlations are compared with experimental data from a previous work of this research group.*

Keywords: *Nucleate boiling, Hydrocarbons, Gasoline fuel, Boiling correlations, Surrogates*

1. INTRODUCTION

In the past decades, considerable effort has been made in terms of modelling nucleate boiling with pure components and mixtures. This phenomenon allows very high heat transfer coefficients and is, therefore, one of the most efficient heat transfer processes, which makes it highly investigated in research centers around the world. Many are the works in the literature that discuss and propose correlations for predicting the heat transfer coefficient, either for pure components (Kiyomura *et al.*, 2017; Gorenflo, 2010; Ribatski and Saiz Jabardo, 2003; Stephan and Abdelsalam, 1980; Rohsenow, 1951) or mixtures (Vinayak Rao and Balakrishnan, 2004; Inoue *et al.*, 1998; Ünal, 1986; Stephan and Körner, 1969). What grounds such research effort are the many applications where nucleate boiling is currently found, such as refrigeration, nuclear energy, space engineering and, more recently, automotive engineering with fuel heating systems for cold-start application (Oliveira *et al.*, 2016).

The prediction of the heat transfer coefficient with pure components is not a simple task and the challenge is even greater with mixtures due to the presence of more conjugated phenomena. Mixture correlations mostly consider at least one phase-equilibrium parameter in the heat transfer coefficient calculation, such as the boiling range (difference between the bubble and dew points) or the compositions of the vapor and liquid phases. When it comes to a mixture with a known composition, these parameters are more easily determined. On the other hand, as discussed in Oliveira *et al.* (2019b), in the case of multicomponent mixtures or fluids whose true composition is impossible to define (such as gasoline, kerosene, diesel and bio-oils), the estimation of the heat transfer coefficient by conventional means is impracticable considering that the phase-equilibrium parameters are not available or cannot be calculated.

As an alternative, by reducing the complexity of the problem and maintaining adequate accuracy, simpler mixtures of fluids called surrogates can be used in order to replace true complex multicomponent mixtures in project calculations. Applying this concept to the prediction of the nucleate boiling heat transfer coefficient, this work analyzes the effect of varying the number of components considered in surrogates for gasoline fuel, limiting the nature of these components to n-alkanes. Moreover, the results obtained for 102 kPa of pressure with well-established nucleate boiling correlations using these surrogates are compared with experimental data from a previous work (Oliveira *et al.*, 2017), where detailed explanation of the experiments can be found.

2. MODEL PRESENTATION

2.1 Distribution function

When dealing with complex multicomponent mixtures, a statistical representation can provide an adequate description of the mixture composition for engineering applications. In this perspective, the use of a smaller number of components to represent the real mixture enables a considerable reduction in the number of equations to be solved in the estimation of the thermophysical properties. Following the considerations developed by Rätzsch and Kehlen (1983), the continuous thermodynamics approach is applied. Thus, the molar concentrations x_i of the number of components N_c considered in the surrogate can be described by means of a probability distribution function (pdf) $f_m(\tau)$, such that:

$$x_i = \int_{\tau_{i-1}}^{\tau_i} f_m(\tau) d\tau \tag{1}$$

where τ is the distribution variable and i is an integer in the range $1 \leq i \leq N_c$.

Along these lines, the distribution function can be written in terms of a property, like the normal boiling point or the molar mass M of the components. Bearing in mind that gasoline, and fossil fuels in general, are predominantly composed of type C_nH_{2n+2} molecules (alkanes), it occurs that the carbon number n is an even more practical choice to use as a distribution variable rather than M. Considering the molecular weight of carbon and hydrogen respectively as 12 kg/kmol and 1 kg/kmol, these two parameters are related by the succeeding equation:

$$M(n) = 14n + 2. \tag{2}$$

Considering the verified utility of the three-parameter gamma distribution function (type 3 of the Pearson system) for characterizing hydrocarbon fuels (Cotterman *et al.*, 1985), the succeeding equation was considered for the distribution function $f_m(n)$:

$$f_m(n) = C_m(n_0, n_f) \frac{(M(n) - \gamma)^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} \exp\left[-\left(\frac{M(n) - \gamma}{\beta}\right)\right] \tag{3}$$

where $n_0 = 5 \leq n \leq n_f = 18$, $\Gamma(\alpha)$ is the Gamma function, $\alpha = 5.7$ and $\beta = 15$, as exposed by Tamim and Hallett (1995), are the parameters that determine the shape of the distribution for gasoline (shown in Fig. 1) and $\gamma = 0$ is the origin of the distribution function. The normalization constant C_m is calculated in order to assure that:

$$\int_{n_0}^{n_f} f_m(n) dn = \sum_{i=1}^{N} x_i = 1. \tag{4}$$

It follows that:

$$C_m(n_0, n_f) = \left\{ \int_{n_0}^{n_f} \frac{(M(n) - \gamma)^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} \exp\left[-\left(\frac{M(n) - \gamma}{\beta}\right)\right] dn \right\}^{-1}. \tag{5}$$

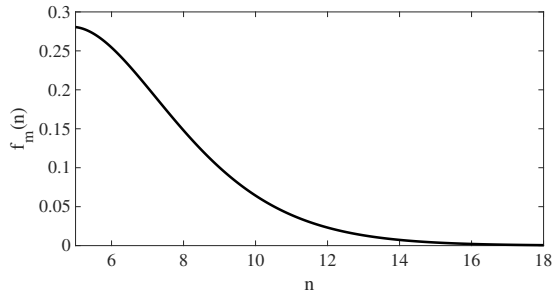

Figure 1. Plot of the probability distribution function versus the number of carbons for gasoline fuel.

In this perspective, the continuous distribution can be replaced by a discrete one, consisting of N_c components with carbon numbers $\overline{n}_i$ as follows:

$$\overline{n}_i = \left[\frac{\int_{n_{i-1}}^{n_i} n f_m(n) dn}{\int_{n_{i-1}}^{n_i} f_m(n) dn} \right] \tag{6}$$

where i is an integer in the range $1 \leq i \leq N_c$ and the brackets represent the rounding of the result to the nearest integer.

At this point, in possession of the molar fractions, the number of carbons of the components and, therefore, the n-alkanes present in the surrogate, it is possible to feed the nucleate boiling correlations for the heat transfer coefficient prediction as a function of the heat flux in the test section. It is important to point out that real gasoline fuels, apart from n-alkanes, contain significant amounts of isoalkanes, alkenes, alkynes, naphthalenes, cycloalkanes, olefins and aromatics. In the present work, these other natures of hydrocarbons are not considered and we limit the N_c components to n-alkanes.

2.2 Nucleate boiling heat transfer

It is usual in heat transfer studies to use the heat transfer coefficient h as the data reduction parameter in order to correlate the heat flux through the heating wall $q_w^{"}$ and the difference between the wall temperature T_w and the fluid temperature. When the fluid is at saturation temperature T_{sat}, which is the case of the present study, h is calculated using the Newton's cooling law:

$$h = \frac{q_w^{"}}{T_w - T_{sat}}. \tag{7}$$

The estimation of the heat transfer coefficient during nucleate boiling have received considerable effort from the heat transfer community in the recent decades. Several parameters affecting this phenomenon have been identified, such as the system pressure, surface finish, fluid temperature, geometry of test section, and others. Considering the facts that no mechanistic equation has been found so far and that the correlations available in the literature are empirical, one must find the correlation that best corresponds to the experimental bench and results under analyses.

In this work, we apply the Ribatski and Saiz Jabardo (2003) correlation for pure n-alkanes heat transfer coefficient calculation because of its great capacity of estimating the heat transfer coefficient with our experimental bench, as exposed in Oliveira *et al.* (2019a). This correlation predicted 91.9% of the experimental data with an accuracy of 30% or better an presented an average overall deviation of 11.2%. For this reason, this correlation is appropriate for the calculation of the heat transfer coefficient h_i for pure components, which is described by the following equation:

$$h_{RiSJ} = f_w p_r^{0.45} \left[-log\left(p_r\right)\right]^{-0.8} Ra^{0.2} M^{-0.5} q_w^{"(0.9-0.3p_r^{0.2})} \tag{8}$$

where p_r is the reduced pressure (the ratio of the system pressure p and the fluid critical pressure p_c), R_a is the average roughness of the heating surface, and M is the fluid molar mass. The parameter f_w depends on the material of the heating surface and is set as 56 in the case of a platinum wire test section (Oliveira *et al.*, 2019a).

Estimating the heat transfer coefficient with mixtures is a more complex process considering the existence of a more volatile component. Therefore, this component evaporates earlier and becomes depleted in the liquid phase near the heating wall, increasing the local saturation temperature and, by consequence, the wall temperature increases (Celata *et al.*, 1994; Stephan and Kern, 2004). Correlations for nucleate boiling with mixtures usually use a degradation factor K to model the heat transfer degradation of an ideal heat transfer coefficient h_{id}:

$$\frac{h}{h_{id}} = \frac{1}{1+K} \tag{9}$$

being h_{id} defined by:

$$\frac{1}{h_{id}} = \sum_{i=1}^{N_{comp}} \frac{x_i}{h_i} \tag{10}$$

where x_i is the molar fraction of the component i in the mixture and h_i the nucleate boiling heat transfer coefficient with the pure component i at the same conditions of the mixture (pressure, heat flux, geometry, material and surface finish). Nucleate boiling correlations for pure components are usually used to estimate h_i if no experimental data is available.

The majority of the mixture correlations use phase equilibrium parameters to estimate the heat transfer degradation, mainly the boiling range ΔT_{bp} and the difference between the vapor and liquid phases compositions. Although most of the correlations were firstly developed based on binary mixtures, some of them can be used as well to multicomponent mixtures. This is the case of correlations based on the boiling range, which can be applied in their original form regardless of the number of components in the mixture (Thome and Shock, 1984; Fujita and Tsutsui, 2004). The mixture correlation applied in the present study is the one proposed by Inoue *et al.* (1998):

$$K_{In} = \frac{h_{id}}{q_w^{"}} \Delta T_{bp} \left[1 - 0.75 exp\left(-0.75 q_w^{"}/10^5\right)\right] \tag{11}$$

which is based on the boiling range ΔT_{bp} so it can be used in their original form. Also, this correlation considers the effect of the heat flux $q_w^{"}$ and the ideal heat transfer coefficient h_{id}. This equation has a simple structure that facilitates

its application in our model and provides virtually the same results with mixtures of hydrocarbons of other correlations based on the boiling range (Thome and Shakir, 1987; Fujita and Tsutsui, 1997).

The mixture boiling range ΔT_{bp} was calculated by estimating the mixture bubble and dew points with the gamma-phi method and the bubble-T algorithm (Poling *et al.*, 2001; Prausnitz *et al.*, 1998). The activity coefficient was calculated using the Dortmund Modified UNIFAC model, which is a fully-predictive group contribution method that provides accurate results of vapor-liquid equilibrium parameters (Lohmann *et al.*, 2001).

3. RESULTS

Table 1 shows examples of surrogates obtained for the applied pdf (Eq. 3), calculating n_i with Eq. 6 and x_i with Eq. 1.

Table 1. Composition of some of the originated surrogates.

Number of components (N_c)	Number of carbons (n_i)	Correspondent n-alkane	Molar fractions (x_i)
1	7	n-heptane	1
2	7	n-heptane	0.9483
	13	n-tridecane	0.0517
4	6	n-hexane	0.7112
	9	n-nonane	0.2371
	13	n-tridecane	0.0453
	16	n-hexadecane	0.0064
12	6	n-hexane	0.2927
	7	n-heptane	0.2418
	8	n-octane	0.1776
	9	n-nonane	0.1193
	10	n-decane	0.0746
	11	n-undecane	0.0439
	12	n-dodecane	0.0248
	13	n-tridecane	0.0135
	14	n-tetradecane	0.0071
	15	n-pentadecane	0.0036
	16	n-hexadecane	0.0018
	17	n-heptadecane	0.0009

Figure 2 shows the experimental data obtained with gasoline at 102 kPa (Oliveira *et al.*, 2017) and the model results for the heat transfer coefficient (h) with the applied correlations as a function of the heat flux (q''_w). As expected, the heat transfer coefficient increases with the heat flux. As one can see from Fig. 2, using a mixture or a single component surrogate brings noticeably different results. The model using only one n-alkane predicts much higher h when compared both to the experimental results and the models using mixtures, regardless of the number of components.

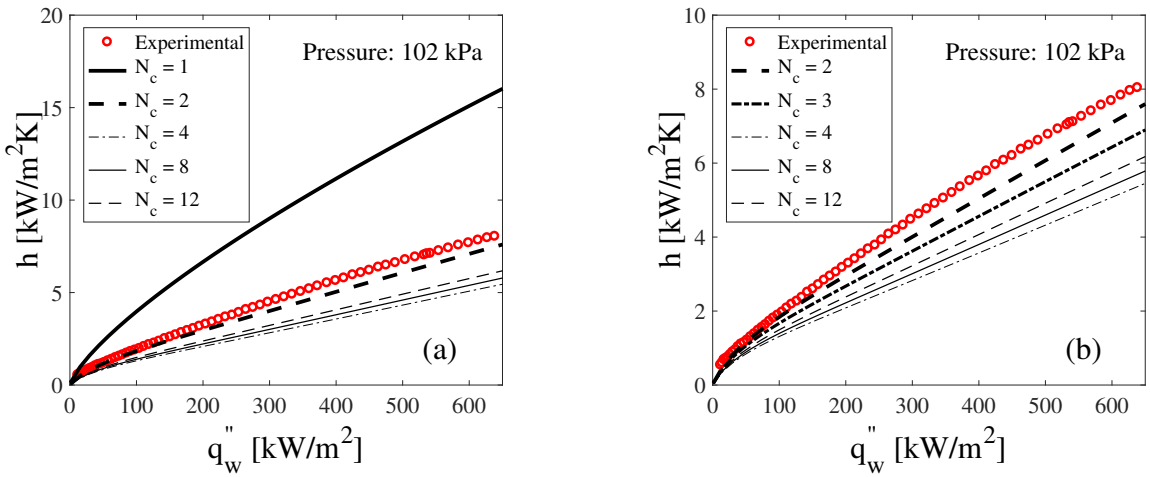

Figure 2. Behavior of the predicted and experimentally determined heat transfer coefficients as a function of the heat flux. (a) with $N_c = 1$; (b) without $N_c = 1$.

It is possible to identify a convergence trend for the heat transfer coefficient with the increase in the number of considered components. Such a trend can be observed in Fig. 3, which presents the overall absolute deviation (OAD) of each surrogate, given by:

$$OAD = \frac{1}{N_{data}} \sum_{i=1}^{N_{data}} \frac{|h_{calc,i} - h_{exp,i}|}{h_{exp,i}} \tag{12}$$

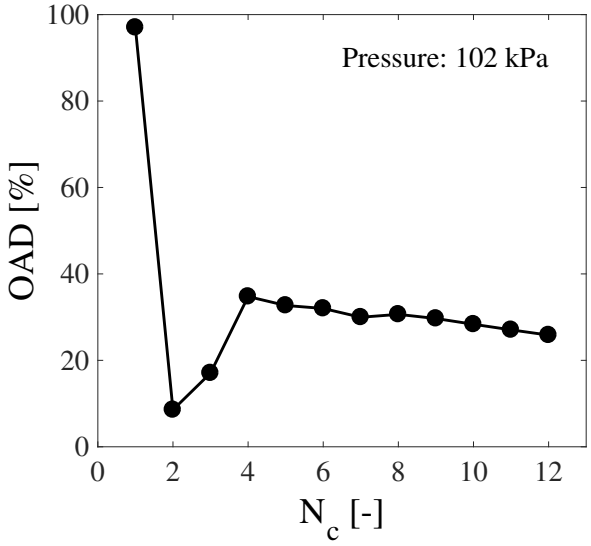

Figure 3. OAD of the heat transfer coefficient calculated using each surrogate for gasoline fuel.

The boiling range is a determinant factor when calculating the ideal heat transfer coefficient degradation in the Inoue *et al.* (1998) correlation. Under these circumstances, the downward trend of the heat transfer coefficient with the increase in the number of components is interrupted from four to five considered components because of a reversal in the trend of the boiling range with the number of components, as seen in Fig. 4.

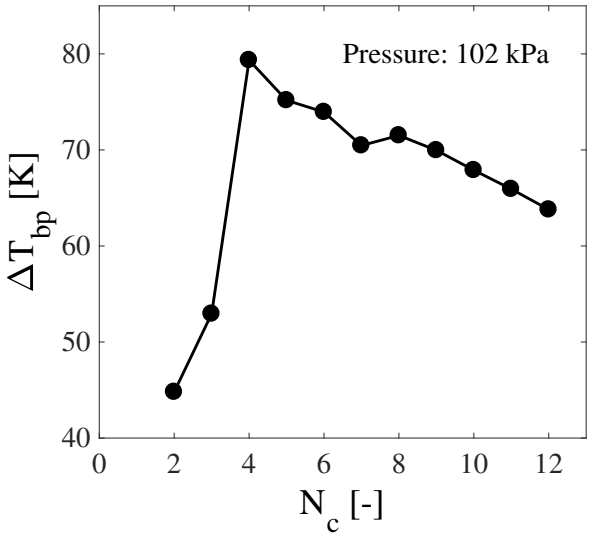

Figure 4. Boiling range as a function of the number of components considered in the surrogates for gasoline.

Figure 5 shows the experimental bubble point temperature obtained for gasoline fuel (Oliveira *et al.*, 2017) and the behavior of the estimated bubble point with the increase in the number of components in the surrogates. It can be observed that such property is overestimated for every surrogate. The reason for this is possibly the limitation of the model to n-alkanes only, indicating that the existence of other classes of hydrocarbons besides n-alkanes may influence the estimation of the properties of the mixture.

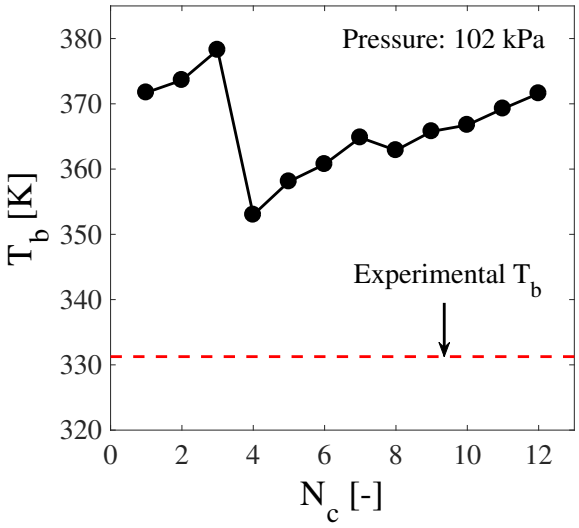

Figure 5. Comparison of the bubble temperatures estimated for each surrogate and the experimentally obtained.

With respect to the impact of the number of components in the calculation time of the heat transfer coefficient, Fig. 6 shows that the calculation time increases linearly with the number of components considered in the mixture. It is of unique importance for engineering projects to find surrogates with the best cost-benefit ratio in terms of accuracy and computational cost. Therefore, future works will investigate whether adding new components and other hydrocarbon natures to the model produces closer results to the experimental ones.

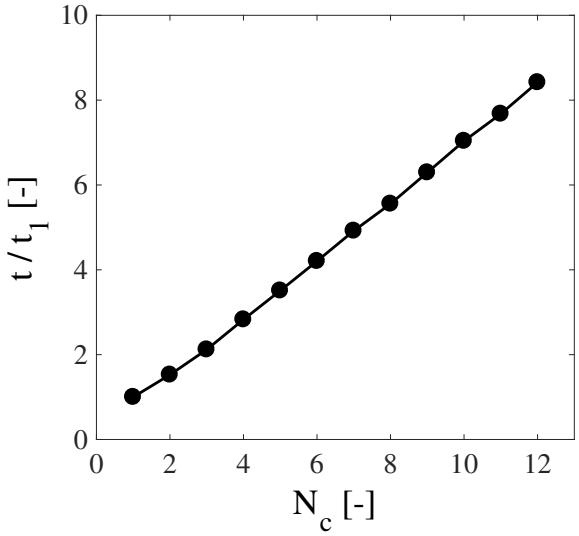

Figure 6. Calculation time normalized by the single component surrogate as a function of the number of components.

4. CONCLUSIONS

The effect of varying the number of components considered in surrogates for gasoline fuel is investigated regarding the estimation of the nucleate boiling heat transfer coefficient. A statistical representation of the composition is applied, limiting its nature to n-alkanes only. The present work brings the results for 102 kPa of pressure and the following conclusions could be made:

- Using a single component to represent gasoline in nucleate boiling calculations is not accurate;
- It is possible to identify a convergence trend for the heat transfer coefficient estimation with the increase in the number of components considered in the surrogates;
- The bubble point of gasoline is not accurately predicted by this method;

- The calculation time increases linearly with the number of components considered in the mixture;

5. ACKNOWLEDGEMENTS

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