

PROPOSAL OF A MATHEMATICAL MODEL OF FOULING IN DISTILLATION PROCESS

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Abstract. Many mathematical models were developed to foresee the fouling process in industrial equipments, but in most cases, they were conducted and applied directly in heat exchangers. The effort to adequate any of these models to fouling phenomena in distillation columns falls in the difficulty of adjusting the constant values attribution. In this work, a model is proposed to foresee the coke fouling formation in distillation columns of heavy fractions of petroleum. The strong tendency of fouling formation on the distillation equipment surfaces is due to the high temperatures involved in the process. The determination of the constants values to be applied to each case is done experimentally determining the chemical kinetics of the conversion of oil into coke and volatile products, assuming the limiting condition of total conversion and the influence of fluid dynamics.

Keywords: Mathematical modelling, Coke, Fouling, Distillation.

1. Introduction

Fouling can be defined as a formation of deposits on heated surfaces, which gradually hinders the heat transfer and increases the flow resistance. The fouling that occurs in petroleum process has been shown as a problem of significant importance in economical and environmental terms (Anderson and Speight, 1999). On the mean time, with the worldwide tendency of petroleum scarcity and the necessity to process heavier fractions of petroleum products, this problem has acquired more scientific attention.

Many mathematical models for prevision of fouling in equipments can be found in the literature. The first model was suggested by Kern and Seaton (1959) and afterwards others were developed but most of them were applied directly to heat exchangers. The effort to adequate any of these models to the fouling phenomena in distillation columns falls in the difficulty of adjusting the constants values attribution (Fiorentin et al., 2004). On the contrary of heat exchangers in which the constants values can be obtained experimentally, the same method can not be applied in distillation columns, because all volumes sections inside the distillation equipments has practically the same temperature. New strategies are required to estimate these constants that permit the correct application of the mathematical models.

Recently, there is a tendency of adapting a specific model for each application. In distillation processes, coke is the specie of fouling that emerges from thermal decomposition of heavy petroleum fractions, which consists of a group of chemical reactions with unclear mechanisms (Abadie, 1997). One of the most accepted recent models of coke formation is suggested by Wiehe (1993), but without any relation to fouling process. A specific mathematical model for distillation fouling is presented in this work as an alternative to already existing ones. The development of this mathematical model is based on the work of Wiehe (1993) and Vatistas (1989) taking into account the physical and chemical factors related to coke formation in vacuum distillation columns, such as the chemical reaction of oil thermal decomposition and the influence of fluid flow dynamics (Bombardelli, 2005a).

2. Influencing Factors

Fouling is a product of a chemical reaction with adhering characteristics that results in a layer of deposited materials, on the internal distillation unit surface, during the time of operation. This layer tends to block the fluid flow inside the equipments, increasing in this way, the pressure drop and decreasing the overall unit efficiency. Among the influencing factors are the fluid composition and conditions that affect the reaction kinetics, in other words, the existence of catalytic substances, temperature and contact conditions between the reactant substances that are strongly influenced by the flow dynamics (Polley et al. 2002). In petroleum processing, it is not always possible to adequate the processed material composition to minimize the fouling formation and considering the importance of the effect of

composition and fluid dynamics on fouling formation, a wider discussion about each of them is presented below.

2.1. Fluid Composition Influences

Petroleum is a complex mixture of organic and inorganic compounds in which predominates the presence of hydrocarbons. Besides the complexity of its structure, the types of petroleum differ a lot from one source to another, which interfere directly in the yield and quality of its products.

It is impossible to classify one type of petroleum by all of its constituent substances. To facilitate this task, the different substances that exist in the petroleum are formed in chemical classes according to its physic-chemical properties. The inorganic fraction is a mixture of mineral salts dissolved in petroleum that must be withdrawn before the refining process takes place to avoid greater problems with mineral fouling. Among the organic substances, occur hydrocarbons, resins and asphaltenes (Bombardelli et al., 2004).

Hydrocarbons are organic compounds formed simply by carbon and hydrogen. They are also designated by oils, which represent the non-polar fraction of petroleum (McCain Jr., 1990). Hydrocarbons can be open paraffinic chain, saturated cyclic chain (naphtas) or aromatic cyclic chain (aromatics). The different grades among these classes of hydrocarbons characterize the type of petroleum in: paraffinic, naphthenic or aromatic (Speight, 1991).

The other substances, of organic nature, existing in petroleum consist of resins and asphaltenes. Both represent the polar fraction of petroleum (McCain Jr., 1990). The pure asphaltenes are solid, non-volatiles, while resins are liquids and are as volatiles as hydrocarbons of the same molecular weight. When the petroleum is fractionated by distillation, the resins are distributed in fractions according to the volatility, while the asphaltenes, due to their solid form, remain in the bottom products. The grades of resins and asphaltenes confer the complexion characteristics for each type of petroleum (McCain Jr., 1990). The soluble fraction that contains all of the oils and the resins receive generic name maltenes (Savage et al., 1985).

In chemical terms, coking is a result of cracking reactions of high molecular weight petroleum substances. These reactions are a form of the mixture substances reaching the thermal-chemical equilibrium point. During cracking, the heavier process breaks up in smaller ones and gives momentary origin to free radicals which require hydrogen to complete the chemical ties emergent from the chain break out (Abadie, 1997). When the fluid does not contain hydrogen granting substances, such as naphtas, the withdrawal of these atoms turn out to occur by the condensation of the aromatic nucleus existing in the mixture (Takatsuka et al., 1989). This type of reaction generates aromatic hydrocarbons with higher molecular weights which tend to assume the properties of the class known by the term coke, while the presence of the hydrogen granting substances decrease the kinetics constant values (Savage et al., 1988).

In a general form, coke formation can be described through the graph shown in Figure 1. This graph presents the thermal decomposition of pure maltenes fraction that was isolated from the asphaltenes and submitted to cracking reaction at a temperature of 400°C. This experiment was conducted by Wiehe (1993).

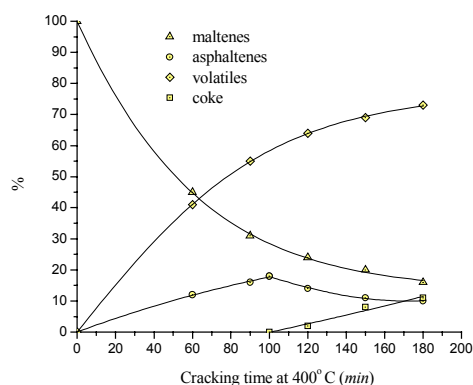


Figure 1 – Thermal decomposition of maltene fraction of a petroleum heavy residue at 400°C.

The described case in Figure 1 is very similar to distillation processes, because theoretically the asphaltene fraction is not distilled, therefore, if fouling occurs in the plates, it would exclusively be due to the maltene fraction decomposition.

The thermal decomposition of maltenes gives origin to three types of products: volatiles, asphaltenes and coke with consequent decrease in the volume of the reactant materials. It is important to note that coke emerges some time after the initial point of the reactions and coincides with a maximum level of asphaltenes obtained. This fact took Wiehe (1993) to conclude that coke emerges by phase separation of the asphaltene fraction from the maltene fraction and this occurs when the degree of saturation is approached. The time period between the reactions start up until the emergence of coke is called the induction period. Many investigators also noted this behaviour (Levinter et al, 1966; Takatsuka et al. 1989). The induction period depends on the temperature and turn out to be nil at a temperature of 450°C (Savage et

al. 1985).

Zhao et al. (2001) also conducted an experiment of decomposition of asphaltenes and the presented conclusion reinforces the models proposed by Wiehe (1993). This means that asphaltenes are not the real precursors of coke if the process was thought as a polymerisation one. The tendency of coke formation resides in the quality of the intermediary products formed during the process.

2.2. Fluid Flow Influences

The analysed mathematical models of fouling forecast can be separated in two groups: models that admit fouling as equilibrium process which involves the decomposition and removal as an independent factors. The other group of mathematical models considers the suppression of the deposition, which is adjusted by some physic-chemical factors such as diffusion, shear stress, etc. The behaviour of the fluid near the fluid-fouling interface is also an important parameter (Taborek et al. 1972). Which of these mentioned groups is more adequate to be used is still an open question.

The fluid effect on the fouling layer in deposition and removal or even in deposition suppression is a complex physic-chemical phenomenon. A simplified form that can be considered is to admit only the influence of the shear stress imposed by the fluid on the adhered particles. Even though the withdrawal of the particles can occur by the action of the fluid shear stress on the fouled surface, it was not established yet how this phase acts parallel to the surface provides a perpendicular lifting force to transport fouling materials from the viscous sub-layer to the turbulent flow region. In front of this uncertainty, Cleaver e Yates (1973) suggested that the removal could be influenced by instabilities that occur in the viscous sub-layer. These instabilities are known by the term *burst* and occur in a similar form to a small localized eddies (Bott, 1995). This movement involves 4 steps: gradual increase in the collision forces intensity, lifting, oscillation and decaying. This additional movement to the friction force is responsible for the removal process because the force intensity during the *burst* events can be extremely high (Vatistas, 1989).

On the other hand, the adherence does not occur in instantaneous mode but needs a period of time to be completed. The adherence between two bodies exists when there is an interface contact that consists of acting forces on these bodies in any direction. Many other phenomenas increase the fluid residence time near the wall. A simple material adherence by the electrostatic polarity action or a simple destabilization of asfaltenes can lead to the formation of adhered small solid particles resulting in mobility decrease and consequently, increasing the fouling possibility. The forces that maintain the bodies adhered on surfaces can be constituted by forces of Van der Waals, DLVO, ion bridging, etc (Oliveira, 1997). The adherence between particles and wall surface is relatively strong according to the degree of the attractive forces intensity and the time involved depends on the kinetics of how these attractive forces are approached (Vatistas, 1989). The velocity and the intensity of the attractive forces can depend on the system temperature, which increases the kinetics rate (Vatistas, 1989).

The most important factor in coke formation is the mean residence time of the fluid in high temperature conditions. Coke formation is by nature a chemical phenomenon, which depends on the temperature and residence time in transforming conditions, but the fouling phenomena can be aided by a complex mechanism of physical nature (Bombardelli et al. 2005b).

The action of the fluid on the fouling layer is an important factor to reduce the probability of coke formation. While the shear stress is distributed uniformly on the surface, the *burst* events occur locally and the existence of two independent phenomenas that control the fouling becomes physically possible, namely: the deposition and removal. Besides they are localized, they have random nature in such a way that they can be interpreted as a parameter for estimating the adherence probability. An outstanding work in his area is due to Vatistas (1989).

3. Considered Hypothesis

For the development of the fouling mathematical model, it was necessary to assume some hypothesis to reduce the complexity of the involved physic-chemical phenomena. Normally, fouling process has induction time period that is a function of temperature. If we accompany a Lagrangian control volume containing heated gas oil in temperature conditions above the point of the initiation of the thermal decomposition, the control volume can be associated to the chemical phenomena showed in Figure 1. The fluid fraction that has residence time period smaller than the coke formation induction time will have in its composition some grade of asphaltenes derived from the reactions, but it will not have coke. On the other hand, it is possible for the fluid fraction, which remains more time to have coke.

Normally, the equipments are designed for the fluid to be processed in a minimum period of time, insufficient for its deterioration, even when submitted to temperature conditions extremely suitable for coke formation. On the mean while, the fluid residence time in the equipment design is considered to be an average period of time, which is not always true for all of the extension of the processed fluid. The existence of the no slip condition besides the equipment internal walls permits the film materials to have a greater residence time than the processing average time. In many cases, sufficient time for material deterioration results in the formation of coke (Bombardelli, 2005a). When this assumed situation exists, fouling occurs by chemical reaction only originated in a thin film on the fluid-wall interface. The last turns out to be fluid-fouling interface after a certain period of time.

The estimation of the film thickness needs the fluid velocity profile to be known. In one of the approximations, we can admit the film thickness formed by the viscous sub-layer, which is a function of the fluid Reynolds number. Because of its slenderness, the film is taken to be the control volume, which can be approximated by a closed chemical reactor, and it can be carried out in laboratories in a similar form to determine the kinetic constants and the solid materials quantity, which a complete reaction can offer.

The internal equipment temperature is assumed to be uniformly distributed and for this reason the reaction can be assumed to have the same kinetics, i.e. the quantities of the produced solid materials are also assumed to be uniformly distributed in all of the equipment extension. In the mean while, if the fluid influence exists, part of the adhered solid materials can be withdrawn in a random way before the chemical reaction that produces coke ends completely.

The concentration does not have any implications because all of the reacted materials result in a solid residues and volatile products, i.e., at the end of the reaction remain only coke and volatile materials. Assuming that all volatile products that suffer volatilisation go to the upper plates and the formed solid material has its mobility reduced each time until it reaches its total conversion. Due to the extreme difficulty in analysing the fluid influence on fouling formation, the adherence probability is introduced as a fouling omission by inserting a mechanism proposed by [Vatistas \(1989\)](#) who assumed in his model the adherence time to be equal to the total conversion time which for the same oil depends only on the temperature.

The solid products originated by the reaction, or precursor, constitute the fouling in its solid state (coke). When approaching its maturation phase, in other words, when it does not reach the hard coke, it suffers the action of the fluid flow and it can be removed in parts. If it remains adhered to the wall surface during the necessary theoretical time for the reaction to be completed, it passes from porous coke to hard coke ([Bombardelli, 2005b](#)).

4. Mathematical Model Development

Thermal decomposition reactions are expected to be of the first order ([Wiehe, 1993](#)), and if they were carried out until the end, result only in coke and volatiles products. The quantity of coke obtained at the end of the reaction with respect to the reacted fluid mass, represented by α , uniformly distributed on the surface of contact between the control volume and the internal wall of the equipment provides a fouling thickness generated by the decomposition when the fluid does not withdraw part of the formed material (fluid dynamic influence).

For first order reactions the formed product quantity is given by Equation (1), in which the rate of mass change is directly proportional to the kinetic constant and to the mass of the reacted fluid. The kinetic constant is a function of temperature according to the Arrhenius' Law ([Hill, 1977](#)).

$$\frac{\Delta m}{\Delta t} = r_i = k.C.V.\rho_f = k.A.e.\rho_f \quad (1)$$

where Δm_i is the coke mass [kg] formed in the time period Δt , k is the chemical kinetic constant in the equipment operation temperature [s^{-1}], C is the reactant concentration [kg_i/kg_f], in the considered case, it is equal to total existing fluid mass in the control volume, A is the relative area of the considered volume [m^2], e is the fluid film thickness [m] and ρ_f is the fluid specific mass [kg/m^3].

If the reaction kinetics change due to any factor, it can be said that the time necessary to produce the same quantity of products follow the relation given by Equation (2). If the reaction kinetics is increased, then, the necessary time to approach the end of the reaction decreases since it is an inversely proportional relation.

$$k.\Delta t = k_{lim}.\Delta t_{lim} \quad (2)$$

where k_{lim} is the chemical kinetics constant [s^{-1}] relative to the condition in which all of the material be transported in volatile and coke products. It is determined experimentally. Δt And Δt_{lim} are, respectively, the reaction time interval and the time interval necessary for complete reaction [s].

Together with the kinetics determination, k [s^{-1}], and from the activation energy E [$kJ/(mol.K)$], the produced solid quantity is obtained, α , with respect to the tested mass and the time period, t_{lim} , for this to occur. α is a function only of the oil composition, resulting always in the same quantity of formed solids once the reaction is completed. The time period necessary for each temperature is determined by Equation (2). For this time interval, the maximum material quantity that can remain as fouling on the contact surface is given by Equation (3).

$$\Delta x_i = \frac{\Delta m_i}{A.\rho_i} = \alpha \cdot e \cdot \frac{\rho_f}{\rho_i} \cdot \frac{k}{k_{lim}} \cdot \frac{\Delta t}{t_{lim}} \quad (3)$$

where Δx_i is the change in fouling thickness [m], occurred during the time interval Δt [s], ρ_i is the density of the formed fouling [kg/m^3]. The conversion velocity varies with temperature and imply directly in the increment of the fouling layer. If the flow does not have any influence on the fouling surface, it can be considered that in each time interval Δt , a layer proportional to α is deposited on the surface A . The proportionality factor is given by the relation between the two terms of the equation and by the control volume thickness e .

Having the operation time Δt from Equation (3) for an infinitesimal time dt , Equation (4) is obtained.

$$\frac{dx_i}{dt} = \alpha \cdot e \cdot \frac{\rho_f}{\rho_i} \cdot \frac{k}{k_{lim} \cdot t_{lim}} \quad (4)$$

but, we know from the Arrhenius' equation that

$$k = k_0 \cdot \exp\left(-\frac{E}{R \cdot T}\right) \quad (5)$$

and $k_{lim} = k_0 \cdot \exp\left(-\frac{E}{R \cdot T_{lim}}\right) \quad (6)$

where E is the activation energy [kJ/mol], T and T_{lim} are the operation temperature and the temperature of the reference point comparison, respectively, normally it is the highest temperature tested in the laboratory. R is the gas constant and k_0 is obtained by a linear adjustment of the kinetic constants (Hill, 1977). Substituting Equations (5) and (6) in Equation (4), results in Equation (7).

$$\frac{dx_i}{dt} = \alpha \cdot e \cdot \frac{\rho_f}{\rho_i} \cdot K \cdot \exp\left(-\frac{E}{R \cdot T}\right) \quad (7)$$

where K is the time constant [s^{-1}], defined by the Equation.

$$\left(K = \frac{1}{t_{lim} \cdot \exp\left(-\frac{E}{R \cdot T_{lim}}\right)} \right) \quad (8)$$

Equation (7) is valid for the conditions of fluid at rest inside the distillation bottom in which a linear fouling increment is expected because both of e , and T , tend to remain constants.

In internal flow, as the fouling thickness, x_i , increases, and fluid velocity also increases causing an immediate action on the thickness e . If turbulent flow is assumed, the flow acting on the fouling layer must be accounted for. When the *burst* events are considered valid, a partial adherence of the formed solid products can be taken into account, as long as the time period for complete reaction does not run out. Introducing the influence of these events as an adherence probability factor, the obtained expression can be written as follows:

$$\frac{dx_i}{dt} = \alpha \cdot P \cdot e \cdot \frac{\rho_f}{\rho_i} \cdot K \cdot \exp\left(-\frac{E}{R \cdot T}\right) \quad (9)$$

where, P is the adherence probability of the particles on the fouling surface. Using the concepts of [Vatistas \(1989\)](#), the adherence probability can be defined by Equation (10). In turbulent flows, the point where the fluid velocity implicates in a residence time greater than the coke formation induction time gives the film thickness e . By simplification this thickness can be assumed to be approximately equal to the depth of the viscous sub-layer ([Paterson & Fryer, 1988](#)).

$$P = (1 - \varepsilon \cdot s)^{t^*} = (1 - \beta)^{t^*} \quad (10)$$

where t^* is the non-dimensional adherence time, ε is the removal efficiency of the *burst events*, s is the unit area,

where the event occurs, it is also considered to be constant for all of the events, in a form that the product ($\varepsilon.s$) results in a unique constant β , whose value is adjusted in a form that the equation has a value approximate to unity when the mean fluid velocity tend to be nil.

The adherence is considered to be complete when the material is totally transformed, the adherence time can be taken as equal to the complete conversion time period, calculated by Equation (2), in a way that the adhesion time can be expressed by Equation (11) (Bombardelli, 2005a). The non-dimensional time, t^* , results from the ratio of the necessary time for adhesion, t_a , and mean time of the *burst* events, t_B , defined by the Equation (Vatistas, 1989).

$$t_a = \frac{k_{lim} \cdot t_{lim}}{k} = \frac{1}{K} \exp\left(\frac{E}{R.T}\right) \quad (11)$$

$$t_B = \frac{100 \cdot \nu}{\vartheta^2} \quad (12)$$

where the term ϑ is the friction velocity [m/s] and ν is the fluid kinematic viscosity [m^2/s]. The ratio of the adhesion period, t_a , and the period t_B results in the Equation (13).

$$t^* = \frac{1}{K} \cdot \frac{\vartheta^2}{100 \cdot \nu} \exp\left(\frac{E}{R.T}\right) = \frac{\tau_w}{100 \cdot K \cdot \mu} \exp\left(\frac{E}{R.T}\right) \quad (13)$$

The friction velocity is a function of shear stress, which is a function of mean flow velocity, u_f . The viscosity is a function of temperature. The viscous sub-layer thickness also is a function of shear stress in a form that both, the non-dimensional time, t^* , and the sub-layer thickness, e , are functions of temperature and fluid velocity, and therefore depends on the piping diameter and fouling thickness. Substituting Equation (10) in Equation (9), the mathematical model can be written in the following form.

$$\frac{dx_i}{dt} = \alpha \cdot (1 - \beta)^{t^*(u_f, T)} \cdot e(u_f, T) \cdot \frac{\rho_f}{\rho_i} \cdot K \cdot \exp\left(-\frac{E}{R.T}\right) \quad (14)$$

where e is the viscous sub-layer thickness [m] and K is the reaction time constant. α is the quantity of coke, in percentage terms, obtained in the integral conversion, β is a value related to the efficiency of the cleanness of the *bursts event*, and t^* is the non-dimensional time, being equivalent to the sum of all *burst* events. For piping, both e and t^* are functions of the fouling layer, because its growth results in increasing the mean fluid velocity, with immediate consequence on the viscous sub-layer thickness and on the adhesion probability.

The model solution is obtained numerically in a sequence of steps. For a given fixed and constant temperature, determine the oil viscosity, the fouling constant time K and the adhesion time t_a . Starting with the mean fluid velocity, determine the shear stress and the friction velocity. These steps can involve the determination of Reynolds number and the friction factor f . With the friction velocity calculate the adhesion probability and the thickness of the reaction volume, obtained in this way the fouling increment for the adapted time step period. This increment influences directly the piping useful diameter and therefore affecting the mean flow velocity resulting in a new condition for the next step of integration (Bombardelli 2005a and Bombardelli et al. 2005c).

5. Results and Discussion

The available mathematical model for fouling in distillation equipments has a drawback due to the difficulty of the determination of the adjusting constants. There are no experimental techniques that ensure the obtainment of these constants in a precise form. In part, this is due to the high temperature levels involved in petroleum industries, which complicates this experimental task.

The suggested mathematical model is presented in a differential equation form that can be solved by numerical integration in function of the operational time resulting in a sum of fouling increments. One of the main advantages of this model is the adequate way to obtain the constants values α , β and K . The application of this model is considered to be valid when fluid residence time in the equipment is a lot lower than the time necessary for the reaction to be completed.

To show part of the usefulness of this model, it was applied to solve numerically some hypothetical situations in which it was included the influence of the fluid dynamics and temperature on the growth of the fouling layer thickness.

Figure 2 presents the fouling layer depth for six years of distillation column operation in function of temperature and

the mean flow velocity. As can be verified, the fouling layer thickness is inversely proportional to the mean flow velocity and directly proportional to the process temperature. The fluid velocity has greater influence in lower temperatures because fouling, in this stage, is a function of adhesion and removal mechanisms and also because the adhesion time is higher at lower temperatures offering, therefore, more time of action on the particles that are not yet totally adhered on the wall surface. It can also be observed that, the existence of a temperature level related with the mean flow velocity in which the fouling would be negligible. This level was presented by Ebert and Panchal (1995) and is known by the term of *threshold condition* and corresponds to the starting limit of fouling when the growth fouling layer turn out to be nil. This point is of a great importance in the determination of the operational conditions that minimize the problem of fouling.

Figure 3 shows two regions: namely fouling region and acceptable fouling region divided by a reference line that represents the maximum level of temperature for a given mean fluid velocity for acceptable fouling. In this figure the acceptable fouling thickness of 5mm is an exaggerated value and is used only for demonstration purposes. As can be noted, if the mean flow velocity was increased from 1.0 to 1.2m/s, the temperature can be increased by 8°C, from 402°C to 412°C, without any change in the expected fouling thickness. This observation demonstrates one of the main objectives of the proposed mathematical model, which is the determination of the critical fouling thickness (Bombardelli 2005c).

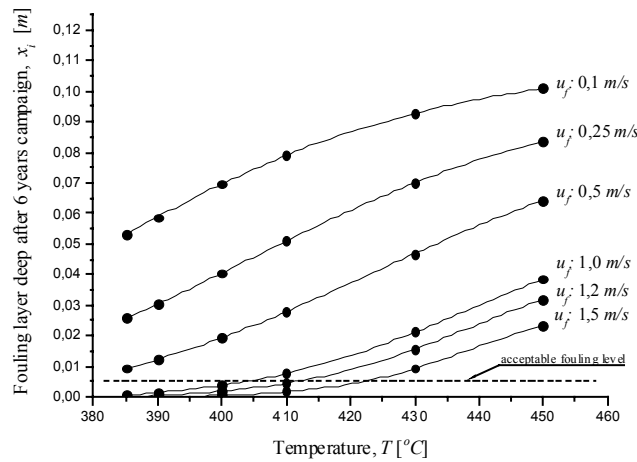


Figure 2 - Variation of fouling layer depth in function of temperature and flow velocity

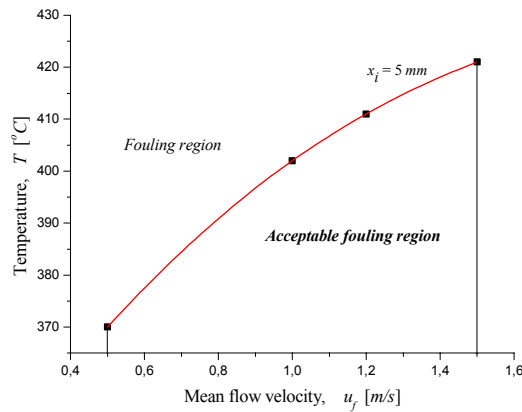


Figure 3- Relation between temperature and mean flow velocity of an acceptable fouling level

6. Conclusions

The developed mathematical model is presented in a differential equation form that can be solved by numerical integration. It is relatively easier to be applied and it offers more adequate way to obtain the constants values α , β and K .

The suggested model has shown promising results, but needs more experimental validation. Both mean flow velocity and operation temperature have great influence on the initial fouling growth and the knowledge of this information results in an economical and environmental advantages.

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8. Responsibility notice

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