On the stationary flow of a waxy crude oil with deposition mechanisms

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Abstract

In this paper we will present a model for the flow of a waxy crude oil in a test loop, taking into account deposition mechanisms due to the high content of paraffin. We will analyse the flow in a non-isothermal condition considering the main rheological parameters depending on the radial coordinate of the pipe. We will formulate the related mathematical problem, which will turn out to be a free boundary problem, and perform a quasi-steady approximation for some of the equations involved. For such approximated problem well posedness is proved.

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1. Introduction

Waxy crude oils are characterized by a high content of paraffin, a mixture of heavy hydrocarbons, called \textit{n}-alkanes, usually ranging from $C_{18}H_{38}$ to $C_{40}H_{82}$. The presence of paraffin can cause severe troubles during all the working processes of these oils.

It is well known that, in special conditions of pressure and temperature, paraffin begins to crystallize and that, once the crystals are formed, they show a strong tendency to aggregate.

The formed agglomerates can turn the oil into a highly viscous material which can be hardly transported through pipelines. Since the temperatures at which paraffin crystallize are not extreme (usually between 10\degree C and 30\degree C), the problem of paraffin crystallization affects most part of waxy crude oils we can find in nature.

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The temperature at which paraffin starts to crystallize is commonly known as Cloud Point, whereas the temperature at which crystals begin to agglomerate is usually called Pour Point. Pour Point is typically 10–15°C lower than the Cloud Point. As showed in [15], for temperatures higher than the Cloud Point, waxy crude oils behave like Newtonian incompressible viscous fluids, while if the temperature is below the Pour Point, their behaviour becomes distinctly non-Newtonian. In the presence of paraffin crystals the oil clearly shows a Bingham behaviour, meaning that there is a yield stress which must be overcome in order to have the oil flowing.

The flow properties of waxy crude oils are actually more complex. The viscosity and the yield stress have a strong dependency on the “thermal history” and on the “mechanical history” of the fluid, and viscosity can be greatly reduced by a continued shear, indicating a kind of “thixotropy”. Our analysis is focused on the flow of a waxy crude oil through an experimental loop. This is essentially a straight portion of a closed cylindrical loop in which the oil is being circulated by a constant applied pressure gradient. In this situation the oil circulating is always the same and no paraffin can be added or removed. Even though the loop system is different from real plants (where fresh oil is continuously supplied to the pipe), it actually provides a good tool for analysing the rheological properties of waxy crude oils in dynamical conditions. In the present paper we will study the dynamics of a waxy crude oil in a non-isothermal situation, taking into account that part of the precipitated paraffin is transported to the pipe wall driven by thermal or mechanical effects. As a consequence, a solid paraffin layer grows at the pipe wall, influencing the whole dynamics. We will formulate a mathematical model for the entire process and, after performing a quasi-steady approximation, we will prove the well posedness of the corresponding free boundary problem.

Different from previous works on this subject (see [5–10]), we will suppose here that the parameters describing the crystalline component in the oil depend also on the radial coordinate of the pipe.

2. Physical description of the problem

Let us consider a portion of a straight cylindrical pipe of radius $R$ and let us call $\vec{e}_z$ the axial unit vector. We want to study the flow of a waxy crude oil, considering that temperature is below the Pour Point and that part of the precipitated paraffin crystals may adhere to the pipe wall, forming a layer of solid material. We will model the flow on the basis of the usual Bingham model for a laminar incompressible fluid and we will assume that the Bingham viscosity and the yield stress both depend on the fraction of crystallized paraffin and on the fraction of agglomerated paraffin.

The deposition rate of paraffin on the pipe wall is due to two main mechanisms: molecular diffusion and shear dispersion. The former is essentially a process due to the presence of a concentration gradient (which is due to the presence of a thermal gradient), while the second results from the “shearing” of the fluid, that basically means that some particles of paraffin tend to migrate towards the pipe wall because of the presence of a velocity gradient.
The model must include an equation for the evolution of the fraction of the agglomerated paraffin and an equation for the evolution of the concentration of crystallized, but not aggregated, paraffin.

3. Physical assumptions

Let us first introduce the following paraffin concentrations which will be useful for describing the crystalline component in the fluid.

- \( C = C(r, t) \), total concentration,
- \( C_d = C_d(r, t) \), concentration of dissolved paraffin,
- \( C_p = C_p(r, t) \), concentration of crystallized paraffin,
- \( C_a = C_a(r, t) \), concentration of aggregated crystallized paraffin,
- \( C_n = C_n(r, t) \), concentration of non-aggregated crystallized paraffin,

where \( r \) is the radial coordinate and \( t \) is time. We assume that all the above concentrations are expressed in \( \text{g/cm}^3 \). We introduce

\[
\beta(r, t) = \frac{C_p(r, t)}{C(r, t)}, \quad \alpha(r, t) = \frac{C_a(r, t)}{C_p(r, t)} \tag{1}
\]

and we call \( \beta \) the crystallization degree and \( \alpha \) the aggregation degree. Since

\[
C(r, t) = C_p(r, t) + C_d(r, t), \quad C_p(r, t) = C_a(r, t) + C_n(r, t) \tag{2}
\]

it follows immediately that \( \alpha \) and \( \beta \) are two non-dimensional parameters taking values between 0 and 1. We assume also that the flow is laminar and incompressible, with a velocity field of the form \( \vec{v} = v(r, t)\hat{e}_z \). We assume that the temperature depends only on \( (r, t) \), and that the crystallization degree \( \beta \) and the concentration \( C_d \) are two known functions of temperature, which will always be supposed below the *Pour Point*. Thus we write

\[
\beta = \beta(T(r, t)), \quad C_d = C_d(T(r, t)) \tag{3}
\]

As we said, below the *Pour Point*, the behaviour of the fluid is comparable to the one of a Bingham fluid (see [4]). Roughly speaking, a Bingham fluid is a non-Newtonian fluid which behaves like a rigid body when the shear stress \( \tau \) is below a certain threshold value \( \tau_0 \), called the yield stress. When \( \tau \) is greater than \( \tau_0 \), the fluid behaves like a viscous fluid. In a system of cylindrical polar coordinates \( (r, \theta, z) \), the constitutive equation for an incompressible laminar Bingham fluid is given by

\[
(\tau - \tau_0)_+ = \eta \left| \frac{\partial v}{\partial r} \right|, \tag{4}
\]

where \( (\cdot)_+ \) stands for the positive part and \( \eta \) is usually referred to as the Bingham viscosity. In what follows we will assume that

\[
\eta = \eta(\alpha, \beta), \quad \tau_0 = \tau_0(\alpha, \beta). \tag{5}
\]
4. Crystalline component

In order to describe the evolution of the agglomerated para/SOn within the fluid, we write the following evolution equation for $\alpha(r,t)$ as in [5]:

$$\frac{d\alpha}{dt} = K_1(T)(1 - \alpha) - K_2(T)\alpha|W(r,t)|.$$  \hspace{1cm} (6)

Here $d/dt$ is the material derivative (meaning we are differentiating w.r.t. time along the path of a fluid particle), $K_1$ and $K_2$ are two positive functions of temperature to be experimentally determined and $W(r,t)$ is the power density dissipated by the viscous forces. Recalling that $\tilde{v} = v(r,t)e_z$, (6) becomes

$$\frac{\partial \alpha}{\partial t} + \frac{\partial \alpha}{\partial r} \cdot \tilde{e}_r \cdot v e_z = K_1(T)(1 - \alpha) - K_2(T)\alpha|W(r,t)|,$$

where $\tilde{e}_r$ is the unit radial vector. It is known that

$$W(r,t) = \frac{\partial v}{\partial r} \left( -\tau_0 + \eta \frac{\partial v}{\partial r} \right).$$ \hspace{1cm} (8)

Thus Eq. (7) becomes

$$\frac{\partial \alpha}{\partial t} = K_1(T)(1 - \alpha) - K_2(T)\alpha \left| \frac{\partial v}{\partial r} \left( -\tau_0 + \eta \frac{\partial v}{\partial r} \right) \right|$$ \hspace{1cm} (9)

which is the evolution equation for the aggregation degree $\alpha$.

5. Thermal field

On the basis of the available data we assume that the thermal conductivity $k$, the thermal capacity $c$ and the density $\rho$ are constant and that they assume the same value in the fluid and in the solid layer (see [3]). Since the velocity field depends only on $r$, no convection is occurring and temperature $T$ will satisfy

$$\frac{\partial T}{\partial t} = \frac{k}{\rho c} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) = 0.$$ \hspace{1cm} (10)

$T$ will always be below the Pour Point if the boundary and initial conditions are specified properly.

6. Deposition mechanisms

In this section we introduce the problem of paraffin deposition on the pipe wall. The two principal mechanisms for paraffin deposition in pipelines are molecular diffusion and shear dispersion (see [1–3,11,12,14,16]). The first involves dissolved paraffin, while
the second crystallized, but not aggregated, paraffin. Molecular diffusion is due to the concentration gradient induced by the temperature gradient. If we indicate with $\tilde{j}_d$ the flux of dissolved paraffin, the mechanism of molecular diffusion can be written by means of Fick’s diffusion equation

$$\tilde{j}_d = -D_d \frac{dC_d}{dT} \frac{\partial T}{\partial r} \tilde{e}_r,$$

(11)

where $D_d$ is the molecular diffusion coefficient. Essentially, $\tilde{j}_d$ expresses the rate at which dissolved paraffin is transported to the wall per unit surface. For what concerns the mechanism of shear dispersion, the usual assumption is that the flux $\tilde{j}_s$ of crystallized, but not aggregated, paraffin is proportional to the concentration of non-aggregated paraffin $C_n$ and to the strain rate $\partial v/\partial r$:

$$\tilde{j}_s = -D_s C_n \frac{\partial v}{\partial r} \tilde{e}_r,$$

(12)

where $D_s$ is the shear dispersion coefficient. The dimensions of $D_d$ are square length over time, whereas $D_s$ is a length. Considering (11) and (12) it is easy to write the evolution equation for the paraffin layer. We assume that the deposit is uniform with thickness $G^{ESC}(t)$. We call $G^{SO}(t) = R - G^{ESC}(t)$ the reduced pipe radius. Since we are dealing with a waxy crude oil circulating in a loop, no paraffin will be added during the flow and, since all the concentrations do not depend on the axial coordinate $z$, we can take a section of length one between, let us say, $z_0$ and $z_0 + 1$, and write the following balance equation:

$$\frac{d}{dt} \left[ \rho \pi (R^2 - \delta^2(t)) \right] = \int_{\Sigma(t)} (\tilde{j}_d + \tilde{j}_s) \cdot \tilde{n} d\sigma,$$

(13)

where $\rho \pi (R^2 - \delta^2(t))$ is the mass of a unit length portion of the deposition layer at some time $t$, $\Sigma(t)$ is the inner surface of the paraffin layer

$$\Sigma(t) = \{(r, \theta, z): r = \delta(t), \theta \in [0, 2\pi], z \in [z_0, z_0 + 1]\}$$

(14)

and $\tilde{n}$ is the outward unit normal to $\Sigma(t)$, that is $\tilde{e}_r$. Eq. (13) tells us that in any portion of fixed length of the pipe the quantity of paraffin must remain constant. Using (11) and (12), Eq. (13) becomes

$$2\rho \delta \dot{\delta} = \int_{\Sigma(t)} \left( D_d \frac{dC_d}{dT} \frac{\partial T}{\partial r} + D_s C_n \frac{\partial v}{\partial r} \right)_{r=\delta(t)} d\sigma,$$

(15)

$$\rho \dot{\delta} = \left( D_d \frac{dC_d}{dT} \frac{\partial T}{\partial r} + D_s C_n \frac{\partial v}{\partial r} \right)_{r=\delta(t)} ,$$

(16)

where $\dot{\delta}$ stands for $d\delta/dt$. Eq. (16) represents the evolution equation of the paraffin layer due to molecular diffusion and shear dispersion.
7. Evolution of $C_n(r, t)$ (non-aggregated paraffin)

If we take a volume $\Omega$ of the fluid, we can write

$$\frac{\partial C_p}{\partial t} + \nabla \cdot (\vec{j}_p) = S_p \quad \text{in } \Omega,$$
(17)

$$\frac{\partial C_d}{\partial t} + \nabla \cdot (\vec{j}_d) = S_d \quad \text{in } \Omega,$$
(18)

where $\nabla \cdot$ is the divergence operator in Cartesian coordinates, $\vec{j}_p$ is the flux of precipitated paraffin, $\vec{j}_d$ is given by (11), $S_p$ is the rate of production of precipitated paraffin and $S_d$ is the rate of production of dissolved paraffin. Adding (17) and (18) we obtain

$$\frac{\partial C}{\partial t} + \nabla \cdot (\vec{j}_d + \vec{j}_p) = S_p + S_d = 0 \quad \text{in } \Omega,$$
(19)

where the last equality is due to the fact that no paraffin is added or removed from the fluid. Hence $S_p = -S_d$, and we have

$$S_p = -\frac{\partial C_d}{\partial t} - \nabla \cdot (\vec{j}_d) = -\frac{\partial C_d}{\partial t} + \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( rD_d \frac{dC_d}{dT} \frac{\partial T}{\partial r} \right) \right],$$

$$= -\frac{dC_d}{dT} \frac{\partial T}{\partial t} + D_d \frac{dC_d}{dT} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + D_d \frac{d^2 C_d}{dT^2} \left( \frac{\partial T}{\partial r} \right)^2.$$
(20)

Hence

$$S_p = -\frac{dC_d}{dT} \left[ \frac{\partial T}{\partial t} - D_d \Delta_r T \right] + D_d \frac{d^2 C_d}{dT^2} \left( \frac{\partial T}{\partial r} \right)^2,$$
(21)

where

$$\Delta_r = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r}$$
(22)

is the Laplacian operator in cylindrical polar coordinates. We assume that the production rate of precipitated paraffin can be split in the following way:

$$S_p = S_a + S_n,$$

where

$$S_a = -\alpha \left\{ \frac{dC_d}{dT} \left[ \frac{\partial T}{\partial t} - D_d \Delta_r T \right] - D_d \frac{d^2 C_d}{dT^2} \left( \frac{\partial T}{\partial r} \right)^2 \right\},$$
(23)

$$S_n = -(1 - \alpha) \left\{ \frac{dC_d}{dT} \left[ \frac{\partial T}{\partial t} - D_d \Delta_r T \right] - D_d \frac{d^2 C_d}{dT^2} \left( \frac{\partial T}{\partial r} \right)^2 \right\}.$$
Here \( S_a \) and \( S_n \) represent the rate of production of aggregated and non-aggregated paraffin, respectively. The concentration \( C_n \) must then satisfy the following equation:

\[
\frac{\partial C_n}{\partial t} + \nabla \cdot \left( -D_s C_n \frac{\partial v}{\partial r} \hat{e}_r \right) = S_n
\]  

(25)

that is

\[
\frac{\partial C_n}{\partial t} - D_s \frac{\partial}{\partial r} \left[ rC_n \frac{\partial v}{\partial r} \right] = (\alpha - 1) \left\{ \frac{dC_d}{dT} \left[ \frac{\partial T}{\partial t} - D_d \Delta_{r} T \right] - D_d \frac{d^2C_d}{dT^2} \left( \frac{\partial T}{\partial r} \right)^2 \right\}
\]

(26)

which is the evolution equation for the concentration \( C_n \).

8. Velocity Field

Recalling that the velocity field has the form \( \vec{v} = v(r,t)\hat{e}_z \), the balance of linear momentum in the fluid phase of the Bingham fluid yields

\[
\rho \frac{\partial v}{\partial t} = f_0 + \frac{1}{r} \frac{\partial}{\partial r} \left[ r \left( -\tau_0 + \eta \frac{\partial v}{\partial r} \right) \right],
\]

(27)

where \( f_0 > 0 \) is the constant driving pressure gradient (see [6]). If we call \( r = s(t) \) the surface separating the rigid core and the fluid part of the Bingham fluid, then, by evaluating the momentum balance of a unit length portion of the rigid core (where \( \tau < \tau_0 \)), we get (see [6])

\[
\rho \frac{\partial v}{\partial t} (s(t), t) = \left[ f_0 - \frac{2\tau_0}{r} \right] \bigg|_{r=s(t)}.
\]

(28)

From (4) we also have that

\[
\frac{\partial v}{\partial r} (s(t), t) = 0.
\]

(29)

9. Mathematical problem

We are now ready to write all the equations that form the mathematical problem including the boundary conditions. We have

\[
\rho \frac{\partial v}{\partial t} = f_0 + \frac{1}{r} \frac{\partial}{\partial r} \left[ r \left( -\tau_0 + \eta \frac{\partial v}{\partial r} \right) \right], \quad s(t) < r < \delta(t), \ t > 0,
\]

(30)

\[
s(0) = s_0, \quad 0 < s_0 < R,
\]

(31)
\[ v(r, 0) = v_0(r), \quad s_0 < r < R, \quad (32) \]
\[ v(\delta(t), t) = 0, \quad t > 0, \quad (33) \]
\[ \frac{\partial v}{\partial r} (s(t), t) = 0, \quad t > 0, \quad (34) \]
\[ \rho \frac{\partial v}{\partial t} (s(t), t) = \left[ f_0 \frac{2\tau_0}{r} \right]_{r=s(t)}, \quad t > 0, \quad (35) \]
\[ \frac{\partial T}{\partial t} - \frac{k}{\rho c} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) = 0, \quad 0 < r < R, \quad t > 0, \quad (36) \]
\[ T(R, t) = \phi(t), \quad t > 0, \quad (37) \]
\[ T(r, 0) = T_0, \quad 0 < r < R, \quad (38) \]
\[ \frac{\partial T}{\partial r} (0, t) = 0, \quad t > 0, \quad (39) \]
\[ \frac{\partial \alpha}{\partial t} = K_1(T)(1 - \alpha) - K_2(T)\alpha \left[ \frac{\partial v}{\partial r} \left( -\tau_0 + \eta \frac{\partial v}{\partial r} \right) \right] \quad 0 < r < \delta(t), \quad t > 0, \quad (40) \]
\[ \alpha(r, 0) = \alpha_0(r), \quad 0 < r < R, \quad (41) \]
\[ \frac{\partial \alpha}{\partial r} (0, t) = 0, \quad t > 0, \quad (42) \]
\[ \rho \dot{\delta} = \left( D_d \frac{\partial C_d}{\partial T} \frac{\partial T}{\partial r} + D_s C_n \frac{\partial v}{\partial r} \right)_{r=\delta(t)}, \quad t > 0, \quad (43) \]
\[ \delta(0) = R, \quad (44) \]
\[ \frac{\partial C_n}{\partial t} - \frac{D_s}{r} \frac{\partial}{\partial r} \left[ rC_n \frac{\partial v}{\partial r} \right] = (\alpha - 1) \frac{\partial C_d}{\partial T} \left[ \frac{\partial T}{\partial t} - D_d A_T \right] \]
\[ + - (\alpha - 1)D_d \frac{\partial^2 C_d}{\partial T^2} \left( \frac{\partial T}{\partial r} \right)^2, \quad 0 < r < \delta(t), \quad t > 0, \quad (45) \]
\[ C_n(r, 0) = C_{n0}(r), \quad 0 < r < R, \quad (46) \]
\[ \frac{\partial C_n}{\partial r} (0, t) = 0, \quad t > 0. \quad (47) \]

Eqs. (30)–(47) form the mathematical problem in its non-stationary formulation. \( v_0(r) \) and \( s_0 \) indicate respectively the initial velocity of the fluid and the initial position of
the surface \( r = s(t) \). Relation (33) expresses the no-slip condition at the layer \( r = \delta(t) \), while (34) and (35) come from (29) and (28). Temperatures \( \phi(t) \) and \( T_0 \) (where \( T_0 \) is supposed constant) represent the temperature at the pipe wall and the initial temperature, both below the Pour Point. Conditions (41), (44) and (46) are the initial data for the aggregation degree \( GVT \), the reduced pipe radius \( GSO \) and the concentration of non-aggregated para/SOn \( C_n \). Relations (39), (42) and (47) express radial symmetry of the functions \( T, GVT \) and \( C_n \). Problems: (30)–(47) is a free boundary problem, in the sense that part of the boundary of the domain for the parabolic equation (30) is unknown. The unknowns are \( v(r, t), s(t), \delta(t), T(r, t), \alpha(r, t) \) and \( C_n(r, t) \). The functions \( r = s(t) \) and \( \delta(t) \) represent the free boundaries. On the basis of the experimental data we will show that a quasi-stationary approximation for some of the equations is feasible. We will perform and justify such an approximation and we will show, under some assumptions on the data, the well posedness of the approximated problem.

10. Quasi-stationary approximation

Let us write problem (30)–(47) in a non-dimensional form. After introducing some characteristic values taken from experimental measurements we will show that some simplifications are possible. Let us rescale all variables as follows:

\[
\begin{align*}
    r &= \tilde{r} R, \\
    t &= \tilde{t}^*, \\
    T &= \tilde{T}(\tilde{r}, \tilde{t}) T^*, \\
    v &= \tilde{v}(\tilde{r}, \tilde{t}) v^*, \\
    \tilde{\alpha}(\tilde{r}, \tilde{t}) &= \alpha(\tilde{r} R, \tilde{t}^*), \\
    \tilde{\beta}(\tilde{T}) &= \beta(\tilde{T} T^*), \\
    \tau_0 &= \tilde{\tau}_0(\tilde{\alpha}, \tilde{\beta}) \tau_0^*, \\
    \eta &= \tilde{\eta}(\tilde{\alpha}, \tilde{\beta}) \eta^*, \\
    C_n &= \tilde{C}_n(\tilde{r}, \tilde{t}) C_n^*, \\
    C_d &= \tilde{C}_d(\tilde{T}) C_d^*, \\
    K_1 &= \tilde{K}_1(\tilde{T}) K_1^*, \\
    K_2 &= \tilde{K}_2(\tilde{T}) K_2^*, \\
    s(t) &= \tilde{s}(\tilde{t}) R, \\
    \delta(t) &= \tilde{\delta}(\tilde{t}) R
\end{align*}
\]

and put

\[
\begin{align*}
    t^* &= \frac{\rho c R^2}{k}, \\
    \tau_0^* &= f_0 R, \\
    v^* &= \frac{f_0 R^2}{\eta^*}, \\
    \tilde{K} &= \frac{K_2^* f_0^2 R^2}{K_1^* \eta^*}, \\
    T^* &= T_0, \\
    C_n^* &= \frac{D_d C_d^*}{D_s v^*},
\end{align*}
\]

where typical values for the rescaling factors are

\[
\begin{align*}
    \rho &= 0.8 \text{ g/cm}^3, \\
    R &= 25 \text{ cm}, \\
    \eta^* &= 0.6 \text{ g/cm s}, \\
    C_n^* &= 0.16 \text{ g/cm}^3, \\
    K_1^* &= 1.25 \times 10^{-4} \text{ s}^{-1}, \\
    K_2^* &= 10^{-6} \text{ Pa}^{-1}, \\
    k &= 0.134 \times 10^{-3} \text{ W K/cm}, \\
    c &= 1920 \times 10^{-3} \text{ J K/gr}, \\
    D_s &= 4.8 \times 10^{-3} \text{ cm}, \\
    D_d &= 0.4 \times 10^{-4} \text{ cm}^2/\text{s}, \\
    T_0 &= 280 \text{ K}, \\
    f_0 &= 2.5 \text{ g/cm}^2 \text{ s}^2.
\end{align*}
\]
Here $K_1^*$ and $K_2^*$ are taken from [7]. Problem (30)–(47) becomes

\[
\left[ \frac{k}{c_\eta^*} \right] \frac{\partial \hat{\nu}}{\partial t} = 1 + \frac{1}{\hat{r}} \frac{\partial}{\partial \hat{r}} \left[ \hat{r} \left( -\tau_0 + \eta \frac{\partial \hat{v}}{\partial \hat{r}} \right) \right], \quad \tilde{s}(\tilde{t}) < \tilde{r} < \delta(\tilde{t}), \quad \tilde{t} > 0, \\
\tilde{s}(0) = \frac{s_0}{R} =: \tilde{s}_0, \quad 0 < \tilde{s}_0 < 1, \\
\tilde{v}(\tilde{r}, 0) = \frac{v_0(\tilde{r}R)}{v^*} =: \tilde{v}_0(\tilde{r}), \quad \tilde{s}_0 < \tilde{r} < 1, \\
\tilde{v}(\tilde{\delta}(\tilde{t}), \tilde{t}) = 0, \quad \tilde{t} > 0, \\
\frac{\partial \hat{\nu}}{\partial \hat{r}}(\tilde{s}(\tilde{t}), \tilde{t}) = 0, \quad \tilde{t} > 0, \\
\left[ \frac{k}{c_\eta^*} \right] \frac{\partial \hat{\nu}}{\partial t}(\tilde{s}(\tilde{t}), \tilde{t}) = \left[ 1 - \frac{2\tau_0}{\hat{r}} \right]_{\tilde{r} = \tilde{s}(\tilde{t})}, \quad \tilde{t} > 0, \\
\frac{\partial \tilde{T}}{\partial \hat{t}} - \left( \frac{\partial^2 \tilde{T}}{\partial \hat{r}^2} + \frac{1}{\hat{r}} \frac{\partial \tilde{T}}{\partial \hat{r}} \right), \quad 0 < \tilde{r} < 1, \quad \tilde{t} > 0, \\
\tilde{T}(1, \tilde{t}) = \phi(\tilde{\delta}^*) \tilde{T}_0 =: \tilde{\phi}(\tilde{t}), \quad \tilde{t} > 0, \\
\tilde{T}(\tilde{r}, 0) = 1, \quad 0 < \tilde{r} < 1, \\
\frac{\partial \tilde{T}}{\partial \hat{r}}(0, \tilde{t}) = 0, \quad \tilde{t} > 0, \\
\left[ \frac{k}{\rho c_\eta^* K_1^*} \right] \frac{\partial \tilde{z}}{\partial \hat{t}} = \tilde{K}_1(\tilde{T})(1 - \tilde{z}) - \tilde{K}_2(\tilde{T}) \tilde{z} \left[ \frac{\partial \hat{v}}{\partial \hat{r}} \right]_{\tilde{r} = \tilde{s}(\tilde{t})}, \quad \tilde{t} > 0, \\
\tilde{z}(\tilde{r}, 0) = \xi_0(\tilde{r}R) =: \tilde{\xi}_0(\tilde{t}), \quad 0 < \tilde{r} < 1, \\
\frac{\partial \tilde{z}}{\partial \hat{r}}(0, \tilde{t}) = 0, \quad \tilde{t} > 0, \\
\left[ \frac{k}{cD_\eta K_1^*} \right] \frac{d \tilde{\delta}}{dt} = \left( \frac{dC_\eta}{\delta^* \tilde{T}} \frac{\partial \tilde{T}}{\partial \hat{r}} + \tilde{C}_n \frac{\partial \hat{v}}{\partial \hat{r}} \right)_{\tilde{r} = \tilde{s}(\tilde{t})}, \quad \tilde{t} > 0, \\
\tilde{\delta}(0) = 1,
\[
\left[ \frac{k\eta^*}{\rho c R^2 D_s f_0} \right] \frac{\partial \tilde{C}_n}{\partial t} + \frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left[ \tilde{r} \tilde{C}_n \frac{\partial \tilde{v}}{\partial \tilde{r}} \right] + \left[ (\tilde{\alpha} - 1) \left( \frac{k}{\rho c D_d} - 1 \right) \right] \frac{d\tilde{C}_d}{d\tilde{T}} \frac{\partial \tilde{T}}{\partial t} + - (\tilde{z} - 1) \frac{d^2 \tilde{C}_d}{d\tilde{T}^2} \left( \frac{\partial \tilde{T}}{\partial \tilde{r}} \right)^2, \quad 0 < \tilde{r} < \tilde{\delta}(\tilde{t}), \quad \tilde{t} > 0,
\]

(63)

\[
\tilde{C}_n(\tilde{r},0) = \frac{C_{n0}(\tilde{r}\tilde{T})}{C_n^*} =: \tilde{C}_{n0}(\tilde{r}), \quad 0 < \tilde{r} < \tilde{\delta}(\tilde{t}),
\]

(64)

\[
\frac{\partial \tilde{C}_n}{\partial \tilde{T}}(0,\tilde{t}) = 0, \quad \tilde{t} > 0.
\]

(65)

Using the rescaling factors we see that

\[
\left[ \frac{k}{\epsilon\eta^*} \right] = 1.16 \times 10^{-3} \ll 1, \quad \left[ \frac{k}{\rho c R^2 k_1^*} \right] = 1.11 \times 10^{-3} \ll 1,
\]

(66)

\[
\left[ \frac{k\eta^*}{\rho c R^2 D_s f_0} \right] = 6.9 \times 10^{-6} \ll 1, \quad \left[ \frac{k}{\rho c D_d} \right] = 0.89 \times 10^{-3} \ll 1,
\]

(67)

\[
\bar{K} = 5.20, \quad \left[ \frac{k}{c D_d C_d^*} \right] = 10.90
\]

(68)

which allows us, for instance, to write Eqs. (48) and (53) in the following way:

\[
1 + \frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left[ \tilde{r} \left( -\bar{\varepsilon}_0 + \eta \frac{\partial \bar{v}}{\partial \tilde{r}} \right) \right] = 0,
\]

(69)

\[
\left[ 1 - \frac{2\bar{\varepsilon}_0}{\tilde{r}} \right] = 0.
\]

(70)

If we integrate (69) between \(\tilde{s}(\tilde{t})\) and \(\tilde{r}\) then, taking into account (70), we have

\[
\frac{\partial \bar{v}}{\partial \tilde{r}}(\tilde{r},\tilde{t}) = \frac{1}{\eta} \left[ \bar{\varepsilon}_0 - \frac{\tilde{r}}{2} \right].
\]

(71)

If we integrate (71) between \(\tilde{r}\) and \(\tilde{\delta}(\tilde{t})\), we obtain

\[
\bar{v}(\tilde{r},\tilde{t}) = \int_{\tilde{r}}^{\tilde{\delta}(\tilde{t})} \frac{1}{\eta} \left[ \frac{\bar{\varepsilon}}{2} - \bar{\varepsilon}_0 \right] d\xi,
\]

(72)

where we recall that \(\bar{\varepsilon}_0\) and \(\eta\) depend on \(\tilde{r}\) through \(\tilde{\alpha}\) and \(\tilde{\nu}(\tilde{T})\). By means of (71) we can also write the following relation:

\[
\frac{\partial \bar{v}}{\partial \tilde{r}} \left[ -\bar{\varepsilon}_0 + \eta \frac{\partial \bar{v}}{\partial \tilde{r}} \right] = \frac{\tilde{r}}{2\eta} \left( \frac{\tilde{r}}{2} - \bar{\varepsilon}_0 \right)
\]

(73)
which has to be substituted in (58). Problem (48)–(65) reduces to
\[ \tilde{s}(\tilde{t}) = [2\tilde{\tau}_0]_{\tilde{r}=\tilde{s}(\tilde{t})}, \quad \tilde{t} > 0, \] (74)
\[ \frac{\partial \tilde{T}}{\partial \tilde{t}} - \left( \frac{\partial^2 \tilde{T}}{\partial \tilde{r}^2} + \frac{1}{\tilde{r}} \frac{\partial \tilde{T}}{\partial \tilde{r}} \right), \quad 0 < \tilde{r} < 1, \tilde{t} > 0, \] (75)
\[ \tilde{T}(1, \tilde{t}) = \tilde{\phi}(\tilde{t}), \quad \tilde{t} > 0, \] (76)
\[ \tilde{T}(\tilde{r}, 0) = 1, \quad 0 < \tilde{r} < 1, \] (77)
\[ \frac{\partial \tilde{T}}{\partial \tilde{r}}(0, \tilde{t}) = 0, \quad \tilde{t} > 0, \] (78)
\[ \tilde{K}_1(\tilde{T})(1 - \tilde{z}) - \tilde{K}\tilde{K}_2(\tilde{T}) \frac{\partial \tilde{T}}{\partial \tilde{r}^2} \frac{\partial \tilde{T}}{\partial \tilde{r}} \tilde{r} - \tilde{\tau}_0 \right| = 0, \quad \tilde{t} > 0, \] (79)
\[ \left( k \frac{cD_d C_d^*}{\rho cD_d} \right) \frac{d \tilde{\delta}}{d \tilde{t}} = \left( \frac{d \tilde{C}_d}{d \tilde{T}} \frac{\partial \tilde{T}}{\partial \tilde{r}} + \tilde{C}_n \frac{\partial \tilde{v}}{\partial \tilde{r}} \right), \quad \tilde{t} > 0, \] (80)
\[ \tilde{\delta}(0) = 1, \] (81)
\[ \frac{1}{\tilde{r}} \frac{\partial}{\partial \tilde{r}} \left[ \tilde{r} \tilde{C}_n \frac{\partial \tilde{v}}{\partial \tilde{r}} \right] + \left[ (\tilde{z} - 1) \left( \frac{k}{\rho cD_d} - 1 \right) \right] \frac{d \tilde{C}_d}{d \tilde{T}} \frac{\partial \tilde{T}}{\partial \tilde{r}} \]
\[ + \frac{1}{\tilde{r}^2} (\tilde{z} - 1) \frac{d^2 \tilde{C}_d}{d \tilde{T}^2} \left( \frac{\partial \tilde{T}}{\partial \tilde{r}} \right)^2 \right] = 0, \quad 0 < \tilde{r} < \tilde{\delta}(\tilde{t}), \quad \tilde{t} > 0, \] (82)
\[ \tilde{C}_n(\tilde{s}) = 0. \] (83)

Condition (83) can be easily derived observing that, from (79), \( \tilde{z} = 1 \) on \( \tilde{r} = \tilde{s}(\tilde{t}) \), hence, from (1) and (2), \( \tilde{C}_n(\tilde{s}) = 0 \).

11. Assumptions on the data

We denote by \( \| \cdot \| \) the usual sup norm. We also define the set
\[ E = [0, 1] \times [0, 1]. \]

We assume that the data of problem (74)–(83) have the following properties:

H1. \( \tilde{K}_1 \) continuously differentiable in \( \tilde{T} \) with \( 0 < \tilde{K}_1_n \leq \tilde{K}_1 \leq \tilde{K}_1_M < \infty \).
H2. \( \tilde{K}_2 \) continuously differentiable in \( \tilde{T} \) with \( 0 < \tilde{K}_2_n \leq \tilde{K}_2 \leq \tilde{K}_2_M < \infty \).
H3. \( \tilde{\beta} \) continuously differentiable in \( \tilde{T} \) with \( d\tilde{\beta}/d\tilde{T} \leq 0 \) and bounded.
H4. \( \tilde{\tau}_0 \in C^1(E) \) with \( 0 < \tilde{\tau}_{0m} \leq \tilde{\tau}_0 \leq \tilde{\tau}_{0r} < \infty \).

H5. \( \tilde{\eta} \in C^1(E) \) with \( 0 < \tilde{\eta}_{m} \leq \tilde{\eta} \leq \tilde{\eta}_{M} < \infty \).

H6. \( \partial \tilde{\tau}_0 / \partial \tilde{\alpha} \geq 0, \partial \tilde{\tau}_0 / \partial \tilde{\beta} \geq 0, \partial \tilde{\eta} / \partial \tilde{\alpha} \geq 0, \partial \tilde{\eta} / \partial \tilde{\beta} \geq 0 \) in \( E \).

H7. \( \tilde{\phi} \in C^1(0, \infty), \quad 0 < 1, \tilde{\phi}(\tilde{t}) < (T_p/T_0) \) and \( -\tilde{\phi}_0 \leq \text{d}\tilde{\phi} / \text{d}\tilde{r} \leq 0, \quad \tilde{\phi}_0 > 0 \).

H8. \( \tilde{\phi}(0) = 1 \),

where \( T_p \) is the Pour Point. Let us define

\[
\begin{align*}
&\left\| \frac{\partial \tilde{\tau}_0}{\partial \tilde{\alpha}} \right\| = \tilde{A}_1, \quad \left\| \frac{\partial \tilde{\tau}_0}{\partial \tilde{\beta}} \right\| = \tilde{B}_1, \quad \left\| \frac{\partial \tilde{\beta}}{\partial \tilde{\alpha}} \right\| = \tilde{C}_1, \quad \left\| \frac{\partial \tilde{\eta}}{\partial \tilde{\alpha}} \right\| = \tilde{A}_2, \quad \left\| \frac{\partial \tilde{\eta}}{\partial \tilde{\beta}} \right\| = \tilde{B}_2,
\end{align*}
\]

where the \( \tilde{A}_j, \tilde{B}_j \) \((j = 1, 2)\) and \( \tilde{C}_1 \) are positive constants. We also assume the following:

H9. \( 1 > \max\{2\tilde{\tau}_{0m}, \tilde{B}_1\tilde{C}_1\tilde{\phi}_0\} \).

H10. \( \tilde{A}_1 < (2\tilde{K}_{1n}\tilde{\eta}_{m})/(\tilde{K}_{2m}\tilde{K}) \).

H11. \( \tilde{A}_2 \leq \tilde{\eta}_{m} \).

H12. \( \tilde{C}_d \) twice continuously differentiable in \( \tilde{T} \) with both derivatives bounded and such that

\[
\frac{d\tilde{C}_d}{d\tilde{T}} \geq 0, \quad (84)
\]

\[
\tilde{S}_d =: \tilde{S}_d(\tilde{T}) = \left( \frac{k}{\rho c D_d} - 1 \right) \frac{d\tilde{C}_d}{d\tilde{T}} \frac{\partial \tilde{T}}{\partial \tilde{T}} - \frac{d^2\tilde{C}_d}{d\tilde{T}^2} \left( \frac{\partial \tilde{T}}{\partial \tilde{T}} \right)^2 \leq 0, \quad (85)
\]

\[
||\tilde{S}_d|| < \frac{2\tilde{\eta}_{m}\tilde{K}_{1n}\rho}{\tilde{\eta}_{M}\tilde{K}_{2m}\tilde{C}_n^*}. \quad (86)
\]

Hypothesis H12 makes sense thanks to estimate (94) on \( \partial \tilde{T} / \partial \tilde{r} \) which we are going to derive in the next section.

12. Estimates on the first derivatives of \( \tilde{T} \)

Let us consider problem (75)–(78). For such a problem standard theorems (see [13]) guarantee the existence and uniqueness of a classical solution \( \tilde{T}(\tilde{r}, \tilde{t}) \). We put \( \tilde{W} = \partial \tilde{T} / \partial \tilde{t} \) and observe that \( \tilde{W} \) solves the following problem:

\[
\frac{\partial \tilde{W}}{\partial \tilde{t}} - \left( \frac{\partial^2 \tilde{W}}{\partial \tilde{r}^2} + \frac{1}{\tilde{r}} \frac{\partial \tilde{W}}{\partial \tilde{r}} \right) = 0, \quad 0 < \tilde{r} < 1, \quad \tilde{t} > 0, \quad (87)
\]

\[
\tilde{W}(1, \tilde{t}) = d\tilde{\phi} / d\tilde{r}, \quad \tilde{t} > 0, \quad (88)
\]

\[
\tilde{W}(\tilde{r}, 0) = 0, \quad 0 < \tilde{r} < 1, \quad (89)
\]

\[
\frac{\partial \tilde{W}}{\partial \tilde{r}}(0, \tilde{t}) = 0, \quad \tilde{t} > 0. \quad (90)
\]
By the maximum principle and hypothesis H7 we have that
\[ \frac{\partial \tilde{T}}{\partial \tilde{t}} \leq 0, \quad \| \frac{\partial \tilde{T}}{\partial \tilde{t}} \| \leq \tilde{\phi}_0. \tag{91} \]

Let us write Eq. (75) in the following form:
\[ \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{T}}{\partial \tilde{r}} \right) = \tilde{r} \frac{\partial \tilde{T}}{\partial \tilde{t}} \tag{92} \]
and integrate between 0 and \( \tilde{r} \). We get
\[ \frac{\partial \tilde{T}}{\partial \tilde{r}} = \frac{1}{\tilde{r}} \int_0^{\tilde{r}} \tilde{\xi} \frac{\partial \tilde{T}}{\partial \tilde{t}} (\tilde{\xi}, \tilde{t}) \, d\tilde{\xi}. \tag{93} \]
From estimates (91) we get
\[ \frac{\partial \tilde{T}}{\partial \tilde{r}} \leq 0, \quad \| \frac{\partial \tilde{T}}{\partial \tilde{r}} \| \leq \frac{\tilde{\phi}_0}{2}. \tag{94} \]

13. Free boundary \( \tilde{r} = \tilde{s}(\tilde{t}) \)

We recall, from (74) and (79), that \( \tilde{s} = 1 \) on \( \tilde{r} = \tilde{s}(\tilde{t}) \). This allows us to write Eq. (74) in the following way:
\[ \tilde{s}(\tilde{t}) - 2\tilde{t}_0(1, \tilde{\beta}(\tilde{T}(\tilde{s}(\tilde{t}), \tilde{t}))) = 0. \tag{95} \]
Under the assumptions we have made, (95) defines the free boundary \( \tilde{r} = \tilde{s}(\tilde{t}) \) implicitly. In order to prove this we consider the function:
\[ \tilde{F}(\tilde{r}, \tilde{t}) = \tilde{r} - 2\tilde{t}_0(1, \tilde{\beta}(\tilde{T}(\tilde{r}, \tilde{t}))) \tag{96} \]

Together with
\[ \frac{\partial \tilde{F}}{\partial \tilde{r}} (\tilde{r}, \tilde{t}) = 1 - 2 \frac{\partial \tilde{\xi}_0}{\partial \tilde{\beta}} \frac{d \tilde{\beta}}{d \tilde{T}} \frac{\partial \tilde{T}}{\partial \tilde{r}}, \tag{97} \]
\[ \frac{\partial \tilde{F}}{\partial \tilde{t}} (\tilde{r}, \tilde{t}) = -2 \frac{\partial \tilde{\xi}_0}{\partial \tilde{\beta}} \frac{d \tilde{\beta}}{d \tilde{T}} \frac{\partial \tilde{T}}{\partial \tilde{t}}. \tag{98} \]
From Hypothesis H9, from the first of (91) and from the first of (94), we have that
\[ \frac{\partial \tilde{F}}{\partial \tilde{r}} (\tilde{s}(\tilde{t}), \tilde{t}) > 0, \quad \frac{\partial \tilde{F}}{\partial \tilde{t}} (\tilde{s}(\tilde{t}), \tilde{t}) \leq 0, \tag{99} \]
thus, by the implicit function theorem, we conclude that, for every \( \tilde{t} > 0 \), there exists a unique function \( \tilde{s}(\tilde{t}) \) such that
\[ \tilde{s}(\tilde{t}) = 2\tilde{t}_0(1, \tilde{\beta}(\tilde{T}(\tilde{s}(\tilde{t}), \tilde{t}))). \tag{100} \]
Further, from H9 and $\tilde{t}_0 > 0$, we also have

$$0 < \tilde{s}(\tilde{t}) < 1, \quad \forall \tilde{t} > 0,$$

(101)

$$\frac{d\tilde{s}(\tilde{t})}{d\tilde{t}} = -\tilde{F}_\tilde{t}(\tilde{s}(\tilde{t}), \tilde{t}) \tilde{F}_\tilde{r}(\tilde{s}(\tilde{t}), \tilde{t}) \geq 0,$$

(102)

where $\tilde{F}_\tilde{t} = \partial\tilde{F}/\partial\tilde{t}$ and $\tilde{F}_\tilde{r} = \partial\tilde{F}/\partial\tilde{r}$. 

### 14. Aggregation degree $\tilde{z}$

So far we have proved that Eq. (100) represents the free boundary $\tilde{r} = \tilde{s}(\tilde{t})$. The next step will be to prove that Eq. (79) defines a unique function $\tilde{z} = \tilde{z}(\tilde{r}, \tilde{t})$ in the domain:

$$D_T = \{\tilde{s}(\tilde{t}) < \tilde{r} < 1, \quad 0 < \tilde{t} < T\}.$$

(103)

Let us consider again the function $\hat{F}(\tilde{r}, \tilde{t})$ defined in (96), which is non-negative in $\bar{D}_T$, because $\hat{F}(\tilde{s}(\tilde{t}), \tilde{t}) = 0$ and $\hat{F}(\tilde{r}, \tilde{t}) \leq 0$, $\hat{F}_\tilde{r}(\tilde{r}, \tilde{t}) > 0$ in $\bar{D}_T$. Let us introduce the function

$$\hat{H}(\tilde{z}, \tilde{r}, \tilde{t}) =: \tilde{r} - 2\tilde{t}_0(\tilde{z}, \beta(\bar{T}(\tilde{r}, \tilde{t})))$

(104)

which is $C^1$ in $[0, 1] \times \bar{D}_T$. Since $\partial\hat{H}/\partial\tilde{z} \leq 0$, then, for all $\tilde{z} \in [0, 1]$, we will have

$$\hat{H}(\tilde{z}, \tilde{r}, \tilde{t}) \geq \hat{H}(1, \tilde{r}, \tilde{t}) = \hat{F}(\tilde{r}, \tilde{t}) \geq 0, \quad (\tilde{r}, \tilde{t}) \in \bar{D}_T.$$

(105)

Notice that $\hat{H}(\tilde{z}, \tilde{r}, \tilde{t}) = 0$ if and only if $(\tilde{r}, \tilde{t}) = (\tilde{s}(\tilde{t}), \tilde{t})$. Inequality (105) tells us that $\partial\hat{H}/\partial\tilde{r}$, given by (71), is non-positive, and allows us to write Eq. (79) in the following manner:

$$\hat{G}(\tilde{z}, \tilde{r}, \tilde{t}) =: \tilde{K}_1(\bar{T})(1 - \tilde{z}) - \tilde{K}\tilde{K}_2(\bar{T})\frac{\tilde{x}_0}{2\tilde{t}_0} \left[ \frac{\tilde{r}}{2} - \tilde{t}_0 \right] = 0.$$

(106)

Let us consider the functions

$$\hat{f}_1(\tilde{z}) =: \tilde{K}_1(\bar{T})(1 - \tilde{z})$$

(107)

$$\hat{f}_2(\tilde{z}) =: \tilde{K}\tilde{K}_2(\bar{T})\frac{\tilde{x}_0}{2\tilde{t}_0} \left[ \frac{\tilde{r}}{2} - \tilde{t}_0 \right]$$

(108)

$(\tilde{r}, \tilde{t})$ being fixed in $\bar{D}_T$. Since $\hat{f}_1$, $\hat{f}_2$ are continuous in $\tilde{z}$ and since $\hat{f}_1(0) > 0$, $\hat{f}_1(1) = 0$ and $\hat{f}_2(0) = 0$, $\hat{f}_2(1) \geq 0$ we have that there must exist at least one point $\tilde{z}_1 \in (0, 1]$ such that $\hat{f}_1(\tilde{z}_1) = \hat{f}_2(\tilde{z}_1)$. We want to prove that under the hypotheses we have made that point is unique. Let us fix a point $(\tilde{r}, \tilde{t}) \in \bar{D}_T$ and let $\tilde{z}_1 \in (0, 1]$ be such
that $\tilde{f}_1(\tilde{x}_1) = f_2(\tilde{x}_1)$. If we show that
\[ \frac{d\tilde{f}_2}{d\tilde{x}}(\tilde{x}_1) > -\tilde{K}_1(\tilde{T}) \]  
then $\tilde{x}_1$ will be the only root of (109). The derivative of $\tilde{f}_2$ w.r.t $\tilde{x}$ is given by
\[ \frac{d\tilde{f}_2}{d\tilde{x}}(\tilde{x}) = \tilde{K} \left[ \tilde{K}_2(\tilde{T}) \frac{\tilde{r}}{2} \left( \frac{\tilde{r}}{2} - \tilde{r}_0 \right) \frac{\partial}{\partial \tilde{x}} \left( \tilde{x} \bigg/ \tilde{h} \right) - \tilde{K}_2(\tilde{T}) \frac{\partial \tilde{r}_0}{\partial \tilde{x}} \tilde{\tilde{r}} \bigg] \right. \]  
(110)
Since $\tilde{f}_1(\tilde{x}_1) = \tilde{f}_2(\tilde{x}_1)$, we have
\[ \tilde{K}\tilde{K}_2(\tilde{T}) \frac{\tilde{r}}{2} \left( \frac{\tilde{r}}{2} - \tilde{r}_0 \right) \frac{\partial}{\partial \tilde{x}} \left( \tilde{x} \bigg/ \tilde{h} \right) = \tilde{K}_1(\tilde{T}) \left( 1 - \tilde{x} \right) \tilde{h} \frac{\partial}{\partial \tilde{x}} \left( \tilde{x} \bigg/ \tilde{h} \right), \]
(111)
where Eq. (111) makes sense because $\tilde{x}_1 \in (0, 1]$. We get
\[ \frac{d\tilde{f}_2}{d\tilde{x}}(\tilde{x}_1) = \left[ \tilde{K}_1(\tilde{T}) (1 - \tilde{x}) \frac{\partial}{\partial \tilde{x}} \left( \tilde{x} / \tilde{h} \right) \frac{\tilde{h}}{\tilde{x}} - \tilde{K}\tilde{K}_2(\tilde{T}) \frac{\partial \tilde{r}_0}{\partial \tilde{x}} \frac{\tilde{\tilde{r}}}{\tilde{h}} \right]_\tilde{x}=\tilde{x}_1. \]
(112)
From assumption H11 we have that
\[ \left( \frac{\partial \tilde{h}}{\partial \tilde{x}} - \frac{\tilde{h}}{\tilde{x}} \right) \bigg|_{\tilde{x}=\tilde{x}_1} < 0, \]
(113)
that is
\[ \left( 1 - \frac{\tilde{x}}{\tilde{h}} \frac{\partial \tilde{h}}{\partial \tilde{x}} \right) \bigg|_{\tilde{x}=\tilde{x}_1} = \left( \tilde{h} \frac{\partial}{\partial \tilde{x}} \left( \tilde{x} / \tilde{h} \right) \right) \bigg|_{\tilde{x}=\tilde{x}_1} > 0. \]
(114)
From assumption H10 we also have
\[ \left[ \frac{\partial \tilde{r}_0}{\partial \tilde{x}} \right] \bigg|_{\tilde{x}=\tilde{x}_1} < \frac{2\tilde{K}_1(\tilde{T})\tilde{h}}{\tilde{K}_2(\tilde{T}) \tilde{K}} \]
(115)
thus
\[ \frac{d\tilde{f}_2}{d\tilde{x}}(\tilde{x}_1) = \left[ \tilde{K}_1(\tilde{T}) (1 - \tilde{x}) \frac{\partial}{\partial \tilde{x}} \left( \tilde{x} / \tilde{h} \right) \frac{\tilde{h}}{\tilde{x}} - \tilde{K}\tilde{K}_2(\tilde{T}) \frac{\partial \tilde{r}_0}{\partial \tilde{x}} \frac{\tilde{\tilde{r}}}{\tilde{h}} \right] \bigg|_{\tilde{x}=\tilde{x}_1} \]
\[ \geq \left[ -\tilde{K}\tilde{K}_2(\tilde{T}) \frac{\partial \tilde{r}_0}{\partial \tilde{x}} \frac{\tilde{\tilde{r}}}{\tilde{h}} \bigg|_{\tilde{x}=\tilde{x}_1} > -\tilde{K}_1(\tilde{T}) \frac{2\tilde{K}_1(\tilde{T})\tilde{K}_2(\tilde{T})\tilde{h} \tilde{\tilde{r}}}{2\tilde{h} \tilde{K} \tilde{K}_2(\tilde{T})} \right. \]  
(116)
which proves inequality (109) for a generic $\tilde{x}_1 \in (0, 1]$ such that $\tilde{f}_1(\tilde{x}_1) = \tilde{f}_2(\tilde{x}_1)$. This implies that for every fixed $(\tilde{r}, \tilde{t}) \in \tilde{D}_T$ there can be only one $\tilde{x}_1 \in (0, 1]$ such that
\[ \tilde{G}(\tilde{x}_1, \tilde{r}, \tilde{t}) = 0, \]
(117)
\[ \frac{\partial \tilde{G}}{\partial \tilde{x}}(\tilde{x}_1, \tilde{r}, \tilde{t}) < 0. \]
(118)
Thus, by the implicit function theorem, we have that \( \tilde{G}(\tilde{x}, \tilde{r}, \tilde{t}) = 0 \) defines implicitly a function \( \tilde{G}(\tilde{r}, \tilde{t}) \in C^1(\tilde{D}_T) \) such that \( 0 < \tilde{x} \leq 1 \) for all \((\tilde{r}, \tilde{t}) \in \tilde{D}_T\). Since

\[
\frac{\partial \tilde{x}}{\partial \tilde{r}} (\tilde{s}(\tilde{t}), \tilde{t}) = \left. \left[ \frac{\tilde{G}_x(\tilde{x}, \tilde{r}, \tilde{t})}{\tilde{G}_r(\tilde{x}, \tilde{r}, \tilde{t})} \right] \right|_{\tilde{x}, \tilde{r}, \tilde{t}} = 0
\]

(119)

where \( \tilde{G} = \partial \tilde{G}/\partial \tilde{x} \) and \( \tilde{G}_r = \partial \tilde{G}/\partial \tilde{r} \), and since

\[
\left[ \frac{\partial \tilde{G}}{\partial \tilde{r}} \right]_{\tilde{x}, \tilde{r}, \tilde{t}} = \left[ \left( \tilde{K}_\tilde{G}(\tilde{T}) \frac{\tilde{r}}{2\tilde{\eta}} \right) \left( \frac{\partial \tilde{r}^0}{\partial \tilde{r}} \frac{\partial \tilde{T}}{\partial \tilde{r}} - \frac{1}{2} \right) \right]_{\tilde{x}, \tilde{r}, \tilde{t}} < 0
\]

(120)

we conclude that

\[
\frac{\partial \tilde{x}}{\partial \tilde{r}} (\tilde{s}(\tilde{t}), \tilde{t}) < 0.
\]

(121)

Even if we have formally found \( \tilde{x}(\tilde{r}, \tilde{t}) \) in the domain \( \tilde{D}_T \), it is important to notice that we are interested only in \((\tilde{r}, \tilde{t}) \) belonging to the following set:

\[
\{(\tilde{r}, \tilde{t}): \tilde{s}(\tilde{t}) < \tilde{r} < \tilde{\delta}(\tilde{t}), \ 0 < \tilde{t} < T\}.
\]

15. Problem for \( \hat{C}_n(\tilde{r}, \tilde{t}) \)

Eq. (82) can be written in the following way:

\[
\frac{\partial}{\partial \tilde{r}} \left[ \tilde{r} \hat{C}_n \frac{\partial \hat{v}}{\partial \tilde{r}} \right] = \tilde{r}(1 - \tilde{x})\tilde{S}_d(\tilde{T}).
\]

(122)

If we integrate Eq. (122) between \( \tilde{s}(\tilde{t}) \) and \( \tilde{r} \) we get

\[
\tilde{r} \hat{C}_n \frac{\partial \hat{v}}{\partial \tilde{r}} = \int_{\tilde{s}(\tilde{t})}^{\tilde{r}} \tilde{\zeta}(1 - \tilde{x})\tilde{S}_d(\tilde{T}) \, d\tilde{\zeta}.
\]

(123)

For any \( \tilde{r} > \tilde{s}(\tilde{t}) \) we have that \( \partial \hat{v}/\partial \tilde{r} < 0 \), thus for any \( \tilde{r} > \tilde{s}(\tilde{t}) \) we can write

\[
\hat{C}_n(\tilde{r}, \tilde{t}) = \frac{1}{\tilde{r} \hat{v}} \int_{\tilde{s}(\tilde{t})}^{\tilde{r}} \tilde{\zeta}(1 - \tilde{x})\tilde{S}_d(\tilde{T}) \, d\tilde{\zeta}.
\]

(124)

If we show that

\[
\lim_{\tilde{r} \to \tilde{s}(\tilde{t})^+} \hat{C}_n(\tilde{r}, \tilde{t}) = 0
\]

(125)

then (124) gives the explicit representation of the solution of problem (82)–(83). Differentiating (71) w.r.t. \( \tilde{r} \) we get

\[
\frac{\partial^2 \hat{v}}{\partial \tilde{r}^2} = \frac{\partial}{\partial \tilde{r}} \left( \frac{1}{\tilde{\tau}_0} \tilde{r} \right) + \frac{1}{\tilde{\eta}} \frac{\partial^2 \tilde{\tau}_0}{\partial \tilde{r}^2}.
\]

(126)
and
\[
\frac{\partial^2 \hat{v}}{\partial \hat{r}^2}(\hat{s}(\hat{t}), \hat{r}) = \left\{ \frac{1}{\hat{\eta}} \left[ \frac{\partial \hat{\xi}_0}{\partial \hat{x}} \frac{\partial \hat{z}}{\partial \hat{r}} + \frac{\partial \hat{\beta}}{\partial \hat{T}} \frac{\partial \hat{\lambda}}{\partial \hat{r}} - \frac{1}{2} \right] \right\}_{(\hat{s}(\hat{t}), \hat{r})} < 0, \tag{127}
\]
where the inequality above comes from H6, (121) and the first of (99). Applying L’Hopital’s rule in order to compute the limit (125) we finally get
\[
\lim_{\hat{r} \to \hat{r}(\hat{t})} \hat{C}_n(\hat{r}, \hat{t}) = \left[ \frac{(1 - \hat{\xi}) \hat{S}_d(\hat{T})}{\hat{r} - \hat{\tau}_0} \right]_{(\hat{s}(\hat{t}), \hat{r})} = 0 \tag{128}
\]
which proves the validity of (125) and entails that (124) is the correct representation for the solution of Cauchy problem (82)–(83). From (79) we have
\[
\hat{r}(1 - \hat{\xi}) = \frac{\hat{K} \hat{K}_2(\hat{T}) \hat{x}^2}{4 \hat{K}_1(\hat{T}) \hat{\eta}} [\hat{r} - \hat{\tau}_0], \tag{129}
\]
where \((\hat{r} - \hat{\tau}_0)\) is a non-decreasing function in \(\hat{r}\). Recalling (86) we get the following inequality:
\[
\hat{C}_n(\hat{r}, \hat{t}) < \frac{\hat{K} \hat{K}_2(\hat{T}) \hat{x}^2 \hat{\eta}_M}{4 \hat{K}_1(\hat{T}) \hat{\eta}_m} \int_{\hat{s}(\hat{t})}^{\hat{r}} \hat{S}_d(\hat{T}) \, d\xi < \frac{\hat{K} \hat{K}_2(\hat{T}) \hat{x}^2 \hat{\eta}_M \| \hat{S}_d \|}{2 \hat{K}_1(\hat{T}) \hat{\eta}_m} < \frac{\rho}{\hat{C}_n}, \tag{130}
\]
which guarantees that the concentration \(C_n\) is always below the density \(\rho\).

16. Problem for \(\hat{\delta}(\hat{t})\)

The last problem we need to solve is the Cauchy problem (80) and (81). We write it as
\[
\frac{d\hat{\delta}}{d\hat{t}} = \hat{h}(\hat{\delta}, \hat{t}), \quad \hat{\delta}(0) = 1, \tag{131}
\]
where \(\hat{h}\), given by
\[
\hat{h}(\hat{\delta}, \hat{t}) = \frac{c D_d \hat{C}_d}{k} \left\{ \left[ \frac{d\hat{C}_d}{d\hat{T}} \frac{\partial \hat{T}}{\partial\hat{r}} \right]_{(\hat{s}(\hat{t}), \hat{r})} + \frac{1}{\hat{\delta}(\hat{t})} \int_{\hat{s}(\hat{t})}^{\hat{r}} \hat{\xi}(1 - \hat{\xi}) \hat{S}_d(\hat{T}) \, d\xi \right\} \tag{132}
\]
is non-positive. Lipschitz continuous and uniformly bounded in \(\hat{\delta}\). Standard theory for ODE guarantees global existence and uniqueness for the solution of (131). A bound for \(|d\hat{\delta}/d\hat{t}|\) is given considering the estimates on the first derivatives of \(\hat{T}\) and the expression of \(\hat{S}_d(\hat{T})\) defined in (85):
\[
\left| \frac{d\hat{\delta}}{d\hat{t}}(\hat{t}) \right| \leq \frac{c D_d \hat{C}_d}{k} \left\{ \left| \frac{d\hat{C}_d}{d\hat{T}} \right| \hat{\phi}_0 + \frac{k}{\rho c D_d} - 1 \left| \frac{d\hat{C}_d}{d\hat{T}} \right| \hat{\phi}_0 + \left| \frac{d^2\hat{C}_d}{d\hat{T}^2} \right| \frac{\hat{\phi}_0^2}{4} \right\} = \hat{C} \hat{\phi}_0, \tag{133}
\]
where \( \tilde{C} \) depends only on the data. By means of (133) we see that \( \tilde{\delta}(\tilde{t}) \) lies above the line:

\[
\tilde{r} = -\tilde{C}\tilde{\phi}_0\tilde{t} + 1,
\]

which intersects the line \( \tilde{r} = 2\tilde{\tau}_{0u}, \) i.e. the sup of \( \tilde{r} = \tilde{s}(\tilde{t}); \) in

\[
\tilde{t} = \frac{1 - 2\tilde{\tau}_{0u}}{\tilde{C}\tilde{\phi}_0}.
\]

Therefore, choosing \( \tilde{\phi}_0 \) sufficiently small, we can have any interval \([0, \tilde{t}_0]\) such that the two boundaries \( \tilde{s}(\tilde{t}) \) and \( \tilde{\delta}(\tilde{t}) \) will never touch each other. Physically this means that the pipe wall must be cooled sufficiently slowly if we want the system not to come to a stop. Eq. (135) tells us how to choose the cooling rate of the pipe wall in order to have a certain time interval in which we are sure that the rigid core will not obstruct the flow of the oil in the pipeline.

### 17. Conclusions

In this paper we have analysed the flow of a waxy crude oil in a laboratory experimental loop. We have modelled the system on the basis of the Bingham model with rheological parameters depending on the fraction of crystallized and aggregated paraffin. We have considered the deposition mechanisms of shear dispersion and molecular diffusion all in a non-isothermal condition. We have written an equation for the evolution of the aggregated paraffin fraction, for the non-aggregated paraffin concentration and for the thermal field. All has been studied in cylindrical geometry and has led to a complex free boundary problem. After having introduced some rescaling factors, we have performed a quasi-stationary approximation for some of the equations involved, remarkably simplifying the problem. Under some hypotheses on the data we have shown that the approximated problem is well posed.

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