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INFLUENCE OF NON-CONDENSABLES ON THE CONDENSATION OF VAPOUR MIXTURES FORMING IMMISCIBLE LIQUIDS

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ABSTRACT

This paper considers condensation of mixed vapours of water and hydrocarbons in the presence of a non-condensable gas, a system that exhibits two liquid phases. A model based on the Maxwell-Stefan equations is developed to calculate the interphase mass and heat transfer fluxes and determine the condensation rates along the height of a vertical condenser tube. Simulations show that a simpler mass transfer model, using effective diffusivities, leads to an overestimation of the condenser area required for a specified condensation duty.

Introduction

Condensation is an operation of great industrial interest. An important problem is that of condensing a mixture of hydrocarbons and steam (water vapour) in the presence of an inert gas such as air, nitrogen or hydrogen. Such systems form two liquid phases when condensed, introducing additional complications in the modelling and design of condensers. There are two main approaches for designing a condenser: the equilibrium models and the non-equilibrium or rate based models. In the first group of models [1,2], equilibrium between the gas and liquid phases is assumed, and the condenser is designed with the so called *condensation curve*, a thermodynamic diagram with temperature-enthalpy co-ordinates together with an appropriate heat transfer correlation. The second group of models [3,4,5] do not make use of the equilibrium assumption and take account of the simultaneous heat and mass transfer processes occurring between the phases. The equilibrium approach has been shown not to be reliable [6], while the non-equilibrium approach gives better results when compared with experimental data [4]. Also, the non-equilibrium approach gives a better insight into the real physical process of condensation, as it takes into account heat and mass transfer rates explicitly, thus providing a theoretical framework in which all the aspects of the process can be taken into account. These non-equilibrium models are also called *film models* (because they are almost invariably based on the film model for interphase mass and heat transfer) and have their origins in the works of Colburn and Hougen [7] and Colburn and Drew [8]. These early works were developed for condensation of binary vapour mixtures. It is now well recognised that for systems containing three or more components we need to take account of diffusional interaction, or coupling, effects. The correct formulation of mass transfer in multicomponent systems is based on the Maxwell-Stefan diffusion equations. The early works of Colburn, Hougen and Drew have been extended for the multicomponent case by using the Maxwell-Stefan equations [3,4,5].

An important issue regarding the non-equilibrium models is to which extent is it necessary to take into account the diffusional interactions explicitly. This question has been previously addressed by Taylor et. al. [4,9] who made simulations using an effective diffusivity model and the complete Maxwell-Stefan film model of Krishna and Standart [10]. Webb [11] published a model for condenser design taking the immiscibility of the condensate phases into account, but no simulation results were presented. Furthermore, the model of Webb [11] does not take account of the influence of inerts, or noncondensable components. The objective of this paper is to develop a model for condensation of vapours of hydrocarbons and water, in the presence of an inert gas and examine the extent to which sophisticated mass transfer models are required to describe the interphase mass and heat transfer process.

Model formulation

We develop a model for condensation inside a vertical tube. The gas flows co-currently with the condensate downward inside the tube, while the coolant flows upwards, i.e. counter-currently, on the outer side; see Fig. 1. The mixture flowing inside is composed by n components: water, n_1 noncondensable components and n_2 hydrocarbons.

The mass balance for the component i in the gas phase, in a slice of a condenser can be written as

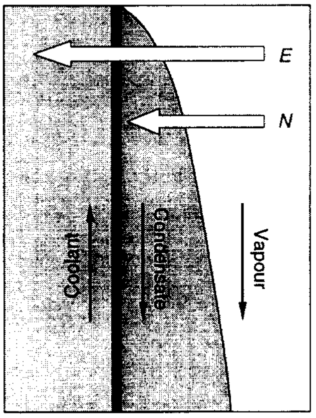

FIG. 1
Condensation inside a vertical tube.

$\frac{dv_i}{dA} = -N_i$; $i = 1,2,...n$. The symbols are defined in in the Nomenclature; see also Fig. 2. The total vapor molar flow is the sum of the component molar fluxes. A similar balance for the liquid phase is $\frac{dl_i}{dA} = N_i$.There are also n-n_1 liquid phase material balances. The total flow of condensate, water and hydrocarbon is $L = \sum l_i$. The energy balance for the gas phase is $\frac{d(VH^V)}{dA} = -E^V$, which relation, simplifies for ideal gas mixtures to $VC_P{}^V \frac{dT^V}{dA} = -q^V$ where q^V is the conductive heat transfer flux, given by $q^V = h_V{}^\bullet(T^V - T^I)$. The heat transfer coefficient is corrected for the influence of the mass transfer according to $h_V{}^\bullet = h_V \Xi_H$. The term h_V is the zero flux heat transfer coefficient, which can be determined from a correlation for turbulent gas flow $Nu = 0.023Re^{0.8}Pr^{1/3}$. The correction factor Ξ_H is the well-known Ackermann correction factor to take account of finite mass transfer rates (for further details see Taylor and Krishna [12]): $\Xi_H = \Phi_H/\exp(\Phi_H) - 1$; $\Phi_H = \sum N_i C_{Pi}/h_V$. Combining above equations we obtain $VC_P{}^V \frac{dT^V}{dA} = -h_V{}^\bullet(T^V - T^I)$. The energy balance for the coolant is $L_C C_P{}^C \frac{dT^C}{dA} = -q^W$ where q^W is the conductive heat transfer flux, given by $q^W = h_0(T^I - T^C)$. Here h_0 represents a combined heat transfer coefficient, including the resistance in the condensate film, in the tube wall and the coolant heat transfer coefficient. T^C is the coolant temperature. The working relation for the coolant temperature variation along the condenser length (area) is $L_C C_P{}^C \frac{dT^C}{dA} = -h_0(T^I - T^C)$.

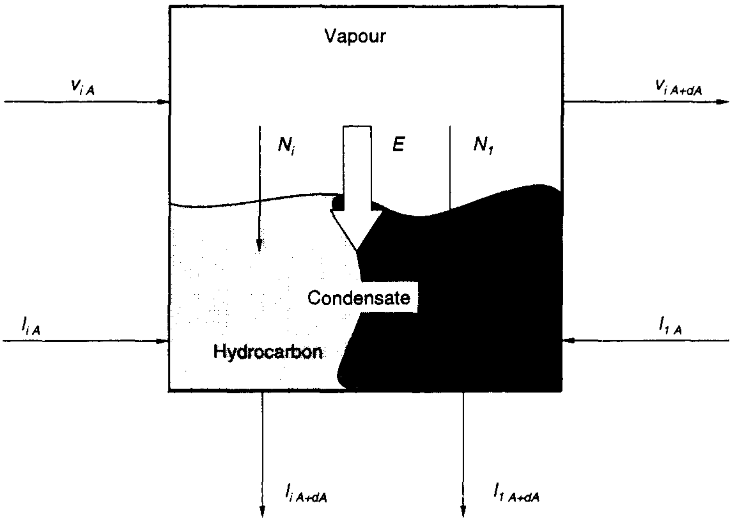

FIG. 2
Fluxes and flows for heterogeneous vapour condensation.

Consider now the phase equilibrium relations. We assume the ideal gas law to apply to the vapour phase. We also postulate complete immiscibility between hydrocarbons and water, and assume that the hydrocarbon mixture obeys Raoult's Law. Each of the two condensed liquid phases exerts its own vapour pressure. This gives for water equilibrium: $y_W{}^I P_T - P_W{}^0 = 0$ and for the hydrocarbon equilibrium: $y_i{}^I - K_i x_i{}^I = 0$ where K_i is simply given by $K_i = P_i^0 / P_T$. There are in total n_2 equilibrium relations for the hydrocarbons and 1 for water.

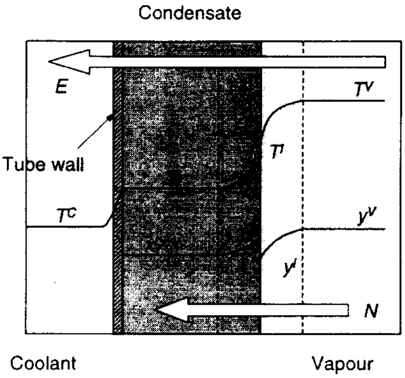

FIG. 3
Temperature and composition profiles at any position in the condenser.

The temperature and composition profiles across the vapour phase, the condensate liquid phase and the coolant are shown in Fig. 3. For the noncondensable components we must have the constraint that there is no transfer flux across the interface, i.e. $N_i = 0$. For determining the transfer fluxes for the condensable species, we write for the gas phase: phase $c_t{}^V [k_V^\bullet](y^V - y^I) + (y^V) N_t - (N) = 0$ where $(N) = (J) + (y^V) N_t$ and $(J) = c_t{}^V [k_V^\bullet](y^V - y^I)$.

In this work we use two different approaches for the calculation of the matrix $[k_V{}^\bullet]$. The first approach is based on the rigorous solution of the Maxwell-Stefan diffusion equations [10,12,13]. In this approach $[k_V{}^\bullet] = [k_0][\Xi_0]$ where the correction factor matrix is $[\Xi_0] = [\Phi][\exp([\Phi]) - [I]]^{-1}$ and the zero flux matrix $[k_0] = [R]^{-1}$. The diagonal elements of $[R]$ are $R_{ii} = y_i / \kappa_{in} + \sum_{\substack{k=1 \\ k \neq i}}^{n} y_k / \kappa_{ik}$ and the off-diagonal elements are given by $R_{ij} = -y_i (1/\kappa_{ij} - 1/\kappa_{in})$. The diagonal elements of the rate factor matrix $[\Phi]$ are defined as $\Phi_{ii} = N_i / c_t \kappa_{in} + \sum_{\substack{k=1 \\ k \neq i}}^{n} N_k / c_t \kappa_{ik}$ whereas the off-diagonal elements of $[\Phi]$ are given by $\Phi_{ij} = -N_i (1/c_t \kappa_{ij} - 1/c_t \kappa_{in})$. We calculate the binary pair mass transfer coefficients κ_{ij} using the Chilton-

Colburn analogy for heat and mass transfer. The correlation valid for turbulent flow ($Re > 10000$) is $Sh_{ij} = 0.023 Re^{0.8} Sc_{ij}^{1/3}$ where the Schmidt and Sherwood numbers are defined, respectively, by $Sc_{ij} = \mu / \text{Đ}_{ij} \rho$ and $Sh_{ij} = \kappa_{ij} d_i / \text{Đ}_{ij}$. The Đ_{ij} are the Maxwell-Stefan diffusivities of the i-j pair in the vapour mixture.

The Maxwell-Stefan equations come into their own when describing a mixture containing species of widely different molar masses. In such cases diffusional interactions, or coupling effects can be expected to be large. In the simulations we performed the molar masses of the components in the vapour phase ranged from hydrogen (MW = 0.002 kg/mol) to n-decane (MW = 0.142 kg/mol), which represents a 70-fold variation. Such large differences in component molar masses results in a large differences in component pair diffusivities. Large differences in component pair diffusivities can give rise to significant coupling effects.

Another approach considered in this work is the simple pseudo-binary form of the mass transfer relations for the fluxes in the vapour phase. The pseudo-binary effective diffusivity can be calculated using the Wilke formula, $D_{i,eff} = (1 - y_i) \Big/ \left[\sum_{\substack{j=1 \\ j \neq i}}^{n} y_j / \text{Đ}_{ij} \right]$. The matrix of zero flux mass transfer coefficients $[k_0]$ is diagonal with the elements $k_{i,eff} = \kappa_{i,eff}$ where the mass transfer coefficients $\kappa_{i,eff}$ are obtained by inserting the effective diffusivitiy $D_{i,eff}$ into Chilton-Colburn equations. The correction factor matrix is also diagonal and can be estimated using the following relations $\Phi_{i,eff} = N_t / c_t \kappa_{i,eff}$ and $\Xi_{i,eff} = \Phi_{i,eff} / \left[\exp(\Phi_{i,eff}) - 1 \right]$. The diagonal $[k_V^{\bullet}]$ matrix of finite flux mass transfer coefficients has the elements $k_{i,eff}^{\bullet} = k_{i,eff} \Xi_{i,eff}$.

The mass transfer resistance in the gas phase is the dominant one in condensation when an inert component is present. It is therefore usual to neglect the mass transfer resistance in the liquid phase and determine the interphase liquid compositions by means of one assumption: completely mixed or completely unmixed liquid. Here we adopt the unmixed liquid, as suggested by Taylor and Krishna [12], because this assumption is the more conservative one, i.e. not leading to underestimation of the condenser area. The equations for the unmixed liquid are $N_i x_R^I - N_R x_i^I = 0$ where the subscript R indicates a reference component. In this work we take the heaviest hydrocarbon as the reference component. There are n_2-1 of this type.

An energy balance around the interphase is also needed. We assume that there is no enthalpy change on mixing and that the condensate subcooling may be ignored. These assumptions lead to $h_V \Xi_H (T^V - T^I) + \sum_{i=1}^{n} N_i (C_{Pi}^V (T^V - T^I) + \lambda_i) - h_0 (T^I - T^C) = 0$.

We must introduce the constraint that the sum of the mole fractions in the vapour phase and in the condensed hydrocarbon liquid phase sum to unity. This constraint is taken care of by two summation equations, one for the vapour side of the interphase $\sum y_i^I - 1 = 0$ and one for the sum of the hydrocarbon compositions in the liquid phase $\sum x_i^I - 1 = 0$.

We have a system of $2n+n_2+1$ of ordinary differential equations. These were integrated using a 4th order Runge-Kutta method with adaptative step size and error control. For the solution of the equations a Newton-Raphson method is implemented, calculating the derivatives in analytical form. The inversion of the Jacobian matrix is done by means of a LU decomposition method. All equations are solved simultaneously without inner and outer loops; this ensures quick convergence.

Simulation results

The vapour mixture consists of hydrocarbons: *n*-hexane (7.5%), *n*-heptane (7.5%), *n*-octane (5%), *n*-nonane (5%) and *n*-decane (5%)) and water vapour (40%). The non-condensables, either hydrogen or nitrogen form the remainder of the vapour phase, i.e. 30 mole %. All the physical properties including diffusivities, vapour pressures, thermal conductivities and densities were estimated as suggested by Reid et. al. [14]. The vapour mixture is condensed inside a vertical tube, 6 m long, of 0.0254 m internal diameter. The system pressure is 20 kPa and the vapour temperature entering the condenser tube is 340 K. The entering coolant temperature is 310 K. For the simulation with hydrogen as inert the total mass flow of the entering vapour mixture is 0.0041 kg/s. For the case with nitrogen as inert, the total mass flow is 0.0049 kg/s.

Figure 4 (a) shows the molar flux, calculated using the rigorous Maxwell-Stefan model, of water and hydrocarbons along the condenser length. It is clear that the fluxes are lower when nitrogen is the inert gas. This is because of the lower diffusivity of nitrogen than hydrogen in the vapour mixture. For the case with hydrogen as inert gas, Fig. 4 (b) compares the fluxes calculated with the Maxwell-Stefan model with those of the simpler Wilke effective diffusivity model. The latter simple model generally calculates lower fluxes. Coupling effects are significant for the case with hydrogen as inert gas and this coupling leads to higher fluxes of hydrocarbons and water !

In Fig. 5 the fraction of the total incoming vapour that is condensed is plotted against the condenser tube length. If, for example, we aim for condensing 50% of the vapour mixture, the Maxwell-Stefan model predicts a lower requirement for condenser area than the Wilke effective diffusivity model. For hydrogen as inert gas the overestimation of the condenser tube area by the Wilke method is 25 % whereas when nitrogen is the inert gas, the overestimation is only 10%.

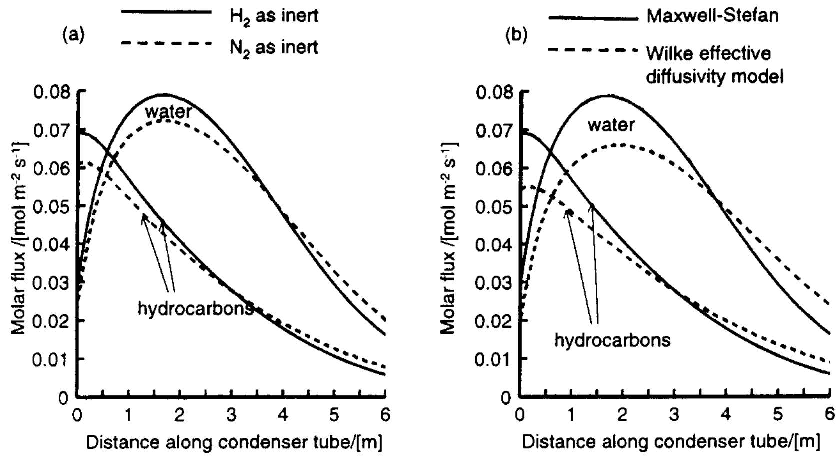

FIG. 4
Transfer fluxes. (a) Influence of inert. (b) Influence of mass transfer model.

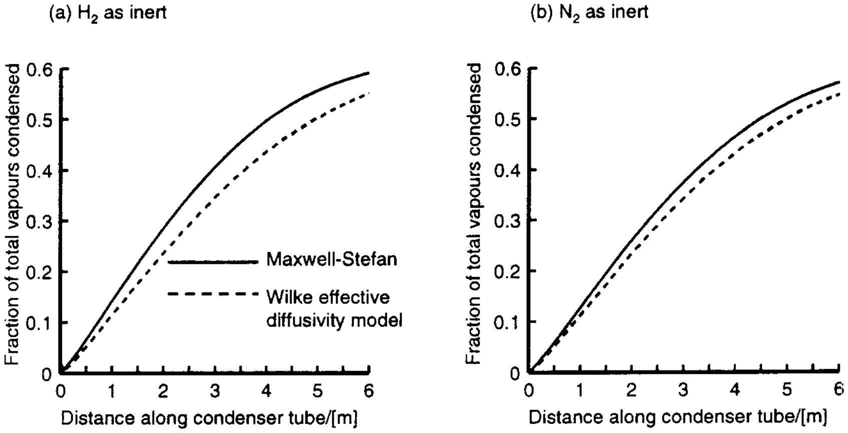

FIG. 5
Fractional vapour condensed.

Conclusions

We have developed a model for heterogeneous condensation of a mixture of hydrocarbon vapours and water in the presence of an inert gas such as hydrogen or nitrogen. When nitrogen is used as inert gas lower fluxes are obtained than when hydrogen is used as inert gas. The effective diffusivity approach to calculation of the mass transfer fluxes overestimates the condenser area requirements by up to 25%. In view of the simplicity of this approach, this approach could be used safely for design purposes, especially when the inert gas is nitrogen (or air). When the inert gas is hydrogen diffusional coupling effects are important and serve to enhance the fluxes and lead to lower condenser area requirements.

Nomenclature

A	Area, m^2
c_t	Total molar concentration, mol m^{-3}
$D_{i,\mathrm{eff}}$	effective diffusivity, m^2 s^{-1}
$Đ$	Maxwell-Stefan diffusivity, m^2 s^{-1}
h	heat transfer coefficient, W m^{-2} K^{-1}
H	Molar enthalpy, J mol^{-1}
$[I]$	Identity matrix, dimensionless
k	mass transfer coefficient, m s^{-1}
$[k]$	matrix of mass transfer coefficients, m s^{-1}
K	Phase equilibrium constant, dimensionless
l	molar flow rate of component in the liquid phase, mol s^{-1}
L	Liquid molar flowrate, mol s^{-1}
N	interphase mass transfer rate, mol s^{-1}
Nu	Nusselt number, dimensionless
P	pressure, Pa
q	conductive heat flux, W m^{-2}
$[R]$	Matrix of inverse mass transfer coefficients, s m^{-1}
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless
T	Temperature, K
u	velocity, m s^{-1}
v	molar flow rate of component in the vapour phase, mol s^{-1}
V	Vapour molar flow rate, mol s^{-1}
x	mole fraction liquid phase component, dimensionless
y	mole fraction vapour phase component, dimensionless

Greek

$[\Phi]$	matrix of dimensionless rate factors, dimensionless
κ	mass transfer coefficient, m s^{-1}
λ	heat of vaporisation, J mol^{-1}
μ	viscosity, Pa s
ρ	mass density, kg m^{-3}
Ξ	correction factor, dimensionless

$[\Xi]$	matrix of correction factors, dimensionless

Subscripts

eff	effective
0	refers to the coolant
H	heat transfer
R	refers to a reference component
V	refers to the vapour phase

Superscripts

0	Refers to pure component
C	Indicates coolant
I	Interface
L	Indicates liquid phase
V	Indicates vapour phase
W	Indicates water
$\bullet$	Indicates finite transfer rates

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