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The micro-explosion strength of emulsified heavy oil droplets in catalytic cracking process

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ABSTRACT

The emulsified feedstock technique applies the secondary atomization mechanism to heavy oil catalytic cracking process, which can significantly improve the atomization of feedstock and result in a more desirable product distribution. A model of micro-explosion strength of emulsion droplets in riser reactor is proposed in this paper. Model calculation shows that the superheat limit of emulsified heavy oil is 307.7 °C at atmospheric pressure, and the micro-explosion strength increases with the size of dispersed water sub-droplets. The theoretical prediction was validated experimentally through feedstock emulsification tests and catalytic cracking experiments. Results indicate that with an increase of the water content in feedstock emulsification, the size of dispersed water sub-droplets in emulsified oil rises, and thus the micro-explosion strength of emulsion droplets in riser reactor increases, which results in a higher light oil yield and lower coke and dry gas yields of catalytic cracking. Compared with pure heavy oil feedstock, the light oil yield rises by 2%, and the yields of coke and dry gas decline by 1.23% and 0.17% respectively for emulsified feedstock at 5% water content.

1. Introduction

In recent years, due to an increasing proportion of residual oil in feedstock for catalytic cracking unit, the operation and development of catalytic cracking process are faced with problems such us high viscosity of feedstock, high carbon residue, and poor atomization in the riser reactor. In order to have a full contact with the catalyst, feed oil should be atomized into micro-droplets rapidly and distributed evenly in the feed zone of the riser reactor by feed nozzles and steam. The atomization of feedstock has a significant impact on the feedstock conversion and product distribution of catalytic cracking, and thus it is extremely urgent to look for a solution to improve the feed atomization.

A series of studies on emulsified diesel combustion show that the secondary atomization of emulsified diesel in compression ignition engines is able to enhance the combustion efficiency considerably and reduce the emission of soot and NO_x [1–3]. This secondary atomization mechanism has been applied to heavy oil catalytic cracking process, which can reduce the droplet size of feed in the riser reactor, enhance the mass and heat transfer, and result in a better product distribution.

Heavy oil, water, and a small amount of surfactant are converted into stable W/O emulsion by high speed shear, wherein the size of dispersed water sub-droplets is about 0.5–15 μm. After preheated and injected into the riser reactor by feed nozzles, the emulsion droplets contact with the high temperature catalyst, then the dispersed water sub-droplets inside boil vigorously. The vapor bubbles grow rapidly and subsequently emulsion droplets are fragmented into many tiny droplets, as is called micro-explosion or secondary atomization. However, at present little attention has been paid to the emulsified feedstock technique from the perspective of micro-explosion [4], there remain several questions to be investigated like whether micro-explosion of emulsion droplets can occur in riser reactor, and how to manipulate the micro-explosion results by controlling process conditions.

The concept of micro-explosion was initially proposed in the studies on the emulsified oil combustion in diesel engines. A few experimental observations on the micro-explosion phenomenon

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Nomenclature

Symbols
D_0 Emulsified droplet diameter (m)
D_1 Water sub-droplet diameter (m)
F Watson characterization factor
J Nucleation rate (nuclei/m^3s)
K Micro-explosion strength (kg/s)
k Boltzmann's constant (J/K)
M Mass of oil phase (kg)
N Total number of molecules in the interfacial region (m^{-3})
P^* Vapor pressure (Pa)
P Ambient pressure (Pa)
T Temperature (K)
Δw^* Free energy of a nucleus of the critical size (J)

Greek
γ Rate of molecules evaporation into a bubble (nuclei/s)
ρ Density (kg/m^3)
σ Surface tension (N/m)

Subscripts
w Water phase
o Oil phase
wo Water/oil interface

in emulsified diesel combustion have been reported in the past few years, wherein the effects of the amount of water and emulsifier on micro-explosion process has been studied [5–11]. However, relevant theoretical studies on micro-explosion are rather limited. Zeng et al. [12] proposed a numerical model of micro-explosion for multicomponent droplets, and determined the size and velocity of sibling droplets by a linear instability analysis, but this model does not fit for oil-water emulsion containing two immiscible phases. Shinjo et al. [13] utilized interface-capturing simulation to investigate the effects of the dispersed water sub-droplet size and location on micro-explosion and puffing. Fu et al. [14] presented a physical hypothesis of the oil membrane formation prior to micro-explosion for an emulsion droplet with a structure of oil-in-water or water-in-oil, and proposed a definition of micro-explosion strength. These researches provides valuable approaches for theoretical studies on micro-explosion, but the effects of emulsifying conditions on micro-explosion results have not been revealed. The micro-explosion in catalytic cracking unit vary from the emulsified oil combustion in diesel engines, since the catalytic cracking feed is much heavier than diesel, and the ambient temperature in the riser reactor is also higher than that in the diesel engine. Thus it is essential to explore the micro-explosion phenomenon in the riser reactor.

In this paper the superheat limit of emulsified heavy oil is first discussed. On this basis a model of micro-explosion strength for an emulsion droplet in the riser reactor is proposed. The effects of water content on the dispersed water sub-droplet size and catalytic cracking product distribution are investigated experimentally to validate theoretical predictions.

2. Theoretical model

2.1. The superheat limit of emulsified heavy oil

Once an emulsion droplet reaches the superheat limit of this emulsion, massive nuclei will generate at the oil-water interface, leading to an explosive boiling. The superheat limit of the emulsion varies from the superheat limit of pure oil or water [15]. According to the homogenous nucleation kinetic theory, the bubble nucleation rate in the water-oil interfacial region is [16]

$$J = (\gamma_w + \gamma_o) N \exp\left(-\frac{\Delta W^*}{kT}\right) \quad (1)$$

where γ_w and γ_o are the rates at which molecules of water and oil evaporate into a bubble respectively, N is the total number of molecules in the water-oil interfacial region, ΔW^* is nucleation free energy, k is the Boltzmann constant, and T denotes temperature.

The nucleation free energy ΔW^* is

$$\Delta W^* = \frac{16}{3}\pi\sigma^3 (P^* - P)^{-2} \quad (2)$$

where P^* is the saturated vapor pressure in the bubble, P is the ambient pressure in the liquid, σ is a generalized surface tension which depends on the relative magnitudes of the surface tension of oil σ_o, the surface tension of water σ_w, and the oil-water interfacial tension σ_{wo}.

There are three possibilities: [16]

I. $\sigma_{wo} > |\sigma_w - \sigma_o|$, the bubble at the interface is lenticular. The generalized surface tension σ is calculated from:

$$\sigma = \left[\sigma_w{}^3\left(\frac{1}{2} - \frac{3}{4}M_w + \frac{1}{4}M_w^3\right) + \sigma_o{}^3\left(\frac{1}{2} - \frac{3}{4}M_o + \frac{1}{4}M_o^3\right)\right]^{\frac{1}{3}} \quad (3)$$

where

$$M_w = \frac{\sigma_w{}^2 - \sigma_o{}^2 + \sigma_{wo}{}^2}{2\sigma_w\sigma_{wo}} \quad (4)$$

$$M_o = \frac{\sigma_o{}^2 - \sigma_w{}^2 + \sigma_{wo}{}^2}{2\sigma_o\sigma_{wo}} \quad (5)$$

II. $\sigma_w \ge \sigma_o + \sigma_{wo}$, the bubble at the interface is spherical resting entirely within oil. The generalized surface tension σ in such case is the surface tension of oilσ_o, which can be estimated as follows [17]:

$$\sigma_o = 0.6737[(T_{co} - T)/T_{co}]^{1.232}/F \quad (6)$$

where T_{co} is the pseudocritical temperature of heavy oil, F is Watson characterization factor.

III. $\sigma_o \ge \sigma_w + \sigma_{wo}$, the bubble at the interface is spherical resting entirely within water. The generalized surface tension σ in such case is the surface tension of waterσ_w, which can be estimated as follows [18]:

$$\sigma_w = 0.2358\left(1 - \frac{T}{T_{cw}}\right)^{1.256}\left[1 - 0.625\left(1 - \frac{T}{T_{cw}}\right)\right] \quad (7)$$

where T_{cw} is the critical temperature of water.

A value of 10^{12} nuclei/(m^3s) is assumed as the threshold nucleation rate corresponding to the onset of homogenous nucleation [19], then the equations above can be solved iteratively to determine the superheat limit of emulsified heavy oil.