CHEMICAL ENGINEERING TRANSACTIONS

VOL. 39, 2014

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong

ISBN 978-88-95608-30-3; **ISSN** 2283-9216

DOI:10.3303/CET1439086

Reactor Design of Microwave Assisted Demetallization of Heavy Crude Oil

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In the recent years with the deeper exploiting of world-wide crude oil, the heavy and poor trend of which is aggravating, inducing the metal contents in the oil increasing rapidly. Vanadium (V) and nickel (Ni) are the most harmful metals to petroleum processing among these metals, which mainly displays poisonous effect to the catalysts of Fluid Catalytic Cracking (FCC) and hydrogenation. The commonly used technologies to remove these metals can be classified into physical method, chemical method and catalytic hydroprocessing method. Hydrodemetallization (HDM) is widely employed in industry. However, the products of HDM reactions can accumulate in the catalyst pores, causing the formation of deposits which end up obstructing those pores irreversibly, blocking access to the catalyst sites and leading to a progressive loss of catalytic activity. Thus the removal of nickel and vanadium from crude oil has become a challenge in petrochemical processing.

This work focuses on these metals removal by using microwave heating technology. A suitable reactor was first developed through numerical simulation technology using COMSOL. It was found that the reactor with a radius of 20 mm shows good coupling with microwaves, and the optimized loading height achieved is 40 mm. Experiments of demetallization were then conducted for Venezuela crude oil using this reactor, the maximum removal rate of 72.4 % and 76.8 % were obtained for Ni and V respectively. However, by using this batch reactor, the temperature distribution is non-uniform within the treated material, a continuous system were therefore developed to overcome the un-even electric field distribution. The reactor was designed as a cylinder with the length of 500 mm, and different crude oil flow rates were simulated, good demetallization rate can be achieved using the same microwave operating conditions.

1. Introduction

With the deeper exploiting crude oil, the heavy and poor trend of which is aggravating, inducing the metal contents in the oil increasing rapidly. Vanadium (V) and nickel (Ni) are the most harmful metals to petroleum processing among these metals, which mainly displays poisonous effect to the catalysts of Fluid Catalytic Cracking (FCC) and hydrogenation. The commonly used technologies removing these metals can be classified into physical method, chemical method and catalytic hydro-processing method. Physical methods include distillation, solvent extraction and filtration. The basic chemical concept of demetallization is to selectively remove the metal from the organic moiety with minimal conversion of remaining petroleum. Whereas catalytic hydro-processing is a hydrogenation process used to remove compounds containing nitrogen, sulphur, oxygen and metals from liquid petroleum fractions. Hydrodemetallization (HDM) means that the molecules containing metals lose these atoms by reactions of hydrogenation, this technology has been successfully employed in industry. However, Ali et al. (2006) have reported that the metals from HDM would accumulate in the catalyst pores, causing the formation of deposits which will finally obstruct those pores irreversibly, blocking access to the catalyst sites and leading to a progressive loss of catalytic activity, other disadvantages such as low demetallization rate, high cost, using of large amount of hydrogen, using high pressure and temperature. Thus the removal of nickel and vanadium from crude oil has become a challenge in petrochemical processing.

Please cite this article as: Shang H., Shi J., Li J., Liu Y., Zhang W., 2014, Reactor design of microwave assisted demetallization of heavy crude oil, Chemical Engineering Transactions, 39, 511-516 DOI:10.3303/CET1439086

Microwave technology has been widely used in oil industry due to its specific heating mechanism (Sobhy and Chaouki, 2010), which attracted a few researchers attention for the metals removal from crude oil by using microwave treatment method. They found that microwave have significant efficiency compared to the corresponding conventional treatment methods. The disadvantages by these researchers can be summarized as the following: they either used very high pressure for HDM process to obtain high removal rate, such as 10 MPa (De Chamorro et al., 2000), or has the limits of high energy cost, low heating efficiency (Wang et al., 2009) and further information in (Wang et al., 2011), long treatment time etc.. Since microwave heating efficiency is determined by the electromagnetic field strength and distribution. To overcome the above shortcomings, microwave heating efficiency should be improved.

It is obvious that the electric field intensity within the sample is of particular importance as it is related to the power density or volumetric adsorption of energy by a squared term. In practice, the electric field strength and distribution are mainly controlled by the design of the microwave heating cavity and the appropriate reactor. It is almost impossible to measure the field strength under process conditions since measurements themselves will perturb the field. Salvi et al. (2008) and further information in (Salvi et al., 2011) have reported their research about successfully simulating continuous flow ballast water, tap water and carboxymethyl cellulose heated by microwave in COMSOL. In this paper batch reactor and a continuous reactor were therefore designed through numerical simulation technology using COMSOL.

2. Methods

2.1 Governing equations

The research began with a relatively simple model with a batch reactor, numerical modelling of which in COMSOL includes coupling of two physics phenomena-electromagnetism and heat transfer. The equations governing the physics phenomena are as the followings.

Electric field distribution in a microwave heating cavity can be calculated by solving the famous Maxwell's equations.

$$\nabla\times\left(\frac{1}{\mu'}\nabla\times\vec{\mathrm{E}}\right)-\frac{\omega^2}{\mathrm{c}}(\varepsilon'-\mathrm{i}\varepsilon'')\vec{\mathrm{E}}=0 \tag{1}$$

Where $\vec{\mathrm{E}}$ is electric field intensity (V/m), ε' is relative permittivity or dielectric constant of a material, ε'' is relative dielectric loss, ω is angular wave frequency ($2\pi f$, rad/s), μ' is the relative permeability and c is the speed of light in free space (3×10^8 m/s).

To calculated the heat generation in dielectric materials by microwave radiation, Eq(2) should be solved.

$$\mathrm{Q}=\sigma\left|\vec{\mathrm{E}}\right|^2=2\pi\varepsilon_0\varepsilon'' f\left|\vec{\mathrm{E}}\right|^2 \tag{2}$$

Where σ is the electrical conductivity of the material (S/m), ε_0 is free space permittivity (8.854×10^{-12} F/m) , and f is the employed frequency (Hz).

The result of Eq(1)- electric field intensity and related material properties will be used when solving Eq(2).

The heat transfer process can be accomplished by calculated Fourier's energy balance equation- Eq(3).

$$\frac{\partial\mathrm{T}}{\partial\mathrm{t}}+\vec{v}\nabla\mathrm{T}=\frac{\kappa}{\rho\mathrm{C_p}}\nabla^2\mathrm{T}+\frac{\mathrm{Q}}{\rho\mathrm{C_p}} \tag{3}$$

Where ρ: material density (kg/m^3), C_p: specific heat (J/kg·K), κ: thermal conductivity (W/m·K), T: temperature (K), $\vec{v}$: velocity vector (m/s) and Q: the volumetric heat generation due to the incident microwave energy (W/m^3).

As the result of Eq(2), Q is the heat source of material acting as a bridge between electromagnetism and heat transfer. Temperature distribution due to heat conduction and convection can be obtained from Eq(3).

The batch reactor system model can be explained by the three above equations. Another physics phenomena-fluid flow will be involved in continuous reactor system. Fluid flow was governed by Navier-Stokes equation-Eq(4) and Eq(5), which describe the momentum balance and continuity.

$$\rho\frac{\partial\vec{v}}{\partial\mathrm{t}}=-\nabla\mathrm{P}+\mu\nabla^2\vec{v}+\rho g \tag{4}$$

$$\nabla \cdot \vec{v} = 0 \tag{5}$$

Where ∇P: the pressure difference (Pa), g: the acceleration due to gravity (m/s^2), and μ: the fluid's viscosity (Pa·s).

2.2 COMSOL Model Establishment

Based on the above governing equations, Microwave heating in RF module was employed to solve the batch reaction system and Laminar Flow of single phase in Fluid Flow module was added to the physics for the continuous reaction system.

Firstly the geometries of microwave reaction systems were generated (Figure 1 is the batch reaction system and Figure 2 is the continuous reaction system). Waveguide (standard WR340), cylindrical cavity (R=35 mm), manual operation electromagnetic field tuner (0 - 100 mm) and reactor were considered for simulation. The size of the batch reactor will be optimized by parameter sweeping, for radius from 17 mm to 23 mm and height from 34 mm and 46 mm. The radius of the continuous flow reactor was 15 mm and the length was 500 mm. To improve the calculating speed and save computing resources, the geometries were cut by the x-z symmetry plane.

Meshes will then be generated. The two geometries were meshed using a free tetrahedral grid and maximum grid size is 6 mm within the reactor and normal size (predefined in COMSOL) for other parts.

Perfect electric conductor condition (default in RF module, $\vec{n} \times \vec{E} = 0$) was adopted for boundary conditions. The left end of the waveguide was a rectangular port, where the microwave with the frequency of 2.45 GHz entered into the reaction system.

The initial or inlet temperature was 70 °C. There is no heat loss through the reactor walls. For continuous flow system, the outlet pressure was atmospheric pressure.

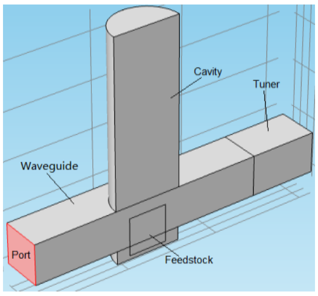


Figure 1: Geometry of batch reaction system

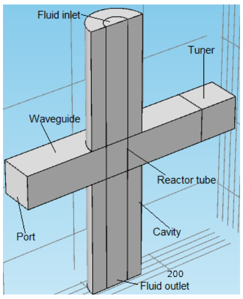


Figure 2: Geometry of continuous reaction system

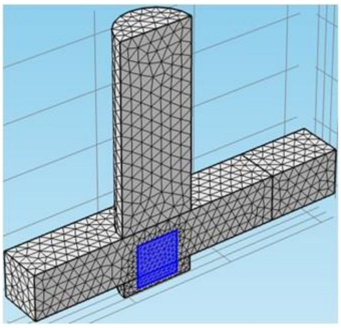


Figure 3: Meshing result of batch reaction system

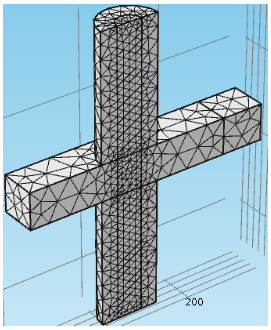


Figure 4: Meshing result of continuous reaction system

Table 1: Properties of feedstock in the simulation

Density	Heat capacity	Relative permittivity (real part)	Relative permittivity (imaginary part)	Thermal conductivity	Ratio of specific heat	Dynamic viscosity at 70 °C	Relative permeability	Electrical conductivity
ρ(kg/m^3)	C_p(J/kg·K)	ε'	ε''	k(W/m·K)	γ	μ(Pa·s)	μ'	σ(S/m)
950	2000	6.76	0.18	65	1.3	0.3	1	0

Feedstock was an emulsion mixture obtained by stirring a mixture of Venezuela crude oil, 10-20 wt % of purified water and 0.5-2 wt % of demetallization agent. The emulsion properties are shown in Table 1.

2.3 Reaction system optimizing process

To design an efficiency system for crude oil demetallization reaction, the goal of more intensive and uniform electric field intensity and less microwave reflection should be achieved. The efficiency can be represented by the reflection coefficient-S_{11} parameter. The coefficient S_{11} is often expressed in decibels and the resulting term, expressed as a positive value, is known as the return loss.

S_{11} parameter is an important factor optimizing of microwave resonant cavity system. Based on its definition, a lower value of S_{11} indicates a better match of the system and the waveguide. A return loss of -20 dB means less than 10 % of microwave was reflected, which is considered to be a good match.

An electromagnetic field tuner (0 - 100 mm) was used at the right end of the waveguide, and electric field distribution can be adjusted by changing its length.

Appropriate tuner lengths for both systems were optimized. For batch reaction system, optimized radius and height of the reactor were achieved by sweeping the optimized parameter. Whilst for continuous flow system, different flow rates were simulated.

3. Results and Discussions

3.1 Simulation and experiment results for batch reaction system

The parameter of tuner length was swept from 0 mm to 100 mm, and the corresponding S_{11} parameter is shown in Figure 5.

Figure 5 clearly indicates that S_{11} parameter varied with tuner length in the form of sine wave. S_{11} parameter changed in a wide range from -37 dB to 5 dB. Therefore, the microwave electric distribution can be adjusted effectively by adjusting the tuner. S_{11} parameter reached the minimum value with the tuner length of 70 mm indicating a good match.

By fixing the tuner length at 70 mm, the reactor radius was then optimized, results are shown in Figure 6.

At the fixed tuner length of 70 mm, the simulation results of S_{11} parameters with different reactor radiuses from -21 dB to -37 dB obviously showed a really good match. in terms of optimized value it should be 20 mm.

Similarly the reactor height was optimized through parameter sweeping. And results suggest that 40 mm was the proper value.

From simulation, the appropriate size for batch reactor was achieved at radius of 20 mm, height of 40 mm. The electric field intensity and distribution in the waveguide, cavity and reactor were then simulated using the optimized geometry (Figures 7 and 8). Temperature increment and distribution after 120 s using 1.5 kW microwave radiation were also calculated in the process (Figure 9).

It can be seen from Figure 7 that electromagnetic wave was mainly distributed in the waveguide and reactor and electric field intensity reached a magnitude of 10^4 V/m. There was nearly no electric filed distribution in the space above the reactor within the cavity, which can improve the efficiency of the whole system.

There was a similar distribution between Z direction of electric field and temperature in batch reactor, which was in accordance with TE10 mode of incident microwave, mainly distributing in Z direction. The temperature was highest (165 °C) in the centre of the reactor and dropped gradually to the reactor wall, where the temperature was 78 °C. Whereas the maximum temperature difference between them was 87 °C, which is thought due to the electric distribution and microwave heating time being short (only 120 s) inducing thermal conductivity was not completed. There is no heat convection in the batch system.

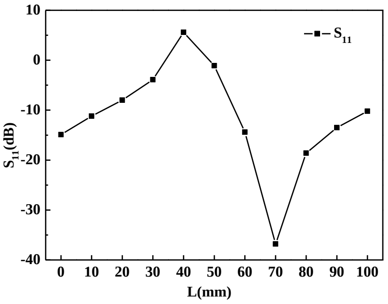


Figure 5: S_{11} parameter varied with tuner length

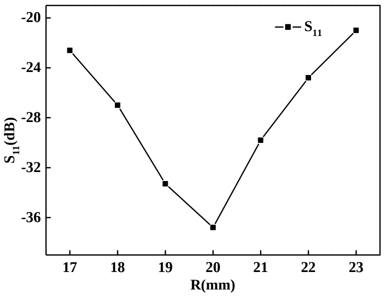


Figure 6: S_{11} parameter varied with the reactor radius

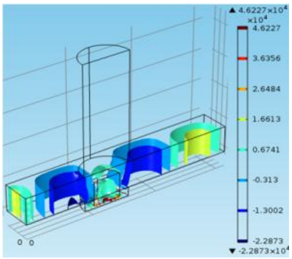


Figure 7: Electric field distribution in waveguide and cavity

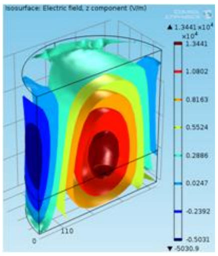


Figure 8: Electric field distribution in batch reactor

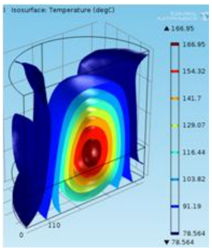


Figure 9: Temperature increment and distribution

Experiments of demetallization were conducted for Venezuela crude oil (Nickel content: 74 μg/g, Vanadium content: 325 μg/g) using the optimized reactor. A maximum removal rate of 72.4 % and 76.8 % were obtained for Ni and V respectively. The metal removal rate was relatively high for such high metal content crude. However, by using this batch reactor, the temperature distribution is non-uniform within the treated material, which limits the demetallization rate. To improve the temperature uniformity, a continuous flow reaction system was designed.

3.2 Simulation and experiment results for continuous flow system

For the continuous system, the material flowed into the reactor at the upper end and out at the lower end of the tube, and the fluid was heated when it flowed through the tube. Similar to the simulation of the batch reaction system, the effects of tuner length and fluid flow rate were investigated by simulating the S_{11} parameter.

It was concluded that the suitable tuner length for continuous flow system was 50 mm, and the flow rate did not affect S_{11} parameter, indicating that the electric field within the reactor did not vary with flow rate.

Unlike the batch reaction system, electric field distributed not only in the waveguide and the middle part of the reaction tube but also in upper and lower part of continuous reactor(Figure 10). In theory, the material will be heated more efficiently and evenly, which can be verified from the temperature distribution (Figure 11). It is obvious, that the thermal convection was improved for fluid flow system, leading a uniform temperature distribution. As cool fresh material entered into the system continuously, the outlet temperature would remain invariable after the system reached a steady state. Thus it is easy to understand that different inlet velocity lead to different steady temperature (Figure 12). With the increase of inlet flow rate, the outlet temperature dropped because of the entering of more cool feedstocks. At the lowest inlet velocity, the outlet temperature was highest, about 230 °C.

As shown in Figure 13, the flow rate was higher in the centre than that close to the wall, which is caused by boundary layer of laminar flow. However, it did not lead to overheating of fluid near the tube wall because the electric field intensity was relatively small near the wall (Figure 14). Figure 15 (b) describes velocity variation along the centre line of tube (the red line in Figure 15 (a)). Due to gravity, there was a velocity increase at the upper part of the reaction tube, and remained the same when gravity equal to viscous force.

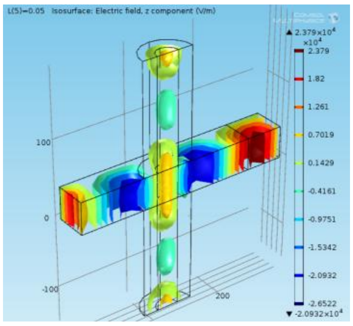


Figure 10: Electric field distribution

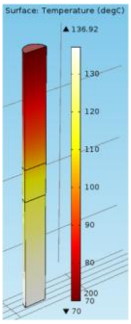


Figure 11: Temperature distribution (v_in=10^{-3} m/s)

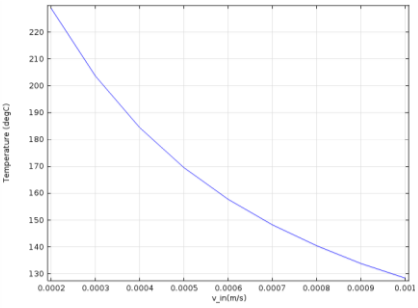


Figure 12: Different limited temperature for different inlet velocity

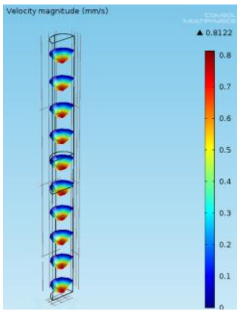


Figure 13: Velocity magnitude in reactor tube

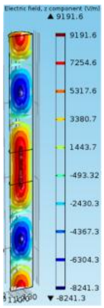
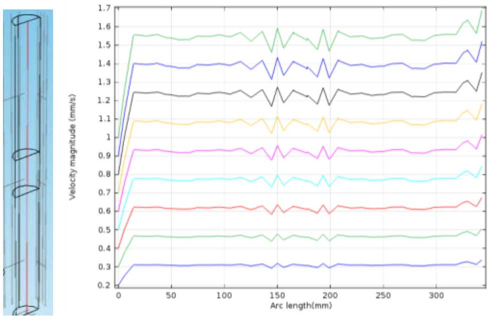


Figure 14: Electric field distribution in reactor



(a) (b)

Figure 15: Flow rate development in the centre line of reactor for different inlet velocity

Experiments of demetallization were also conducted within continuous reaction system for the same oil as batch reactor. Better results were achieved compared to those from batch reactor system, with the maximum Ni and V removal rate of 76.8 % and 83.2 % respectively at the flow rate of 70.65 mL/min (corresponding resident time of 5 min), showing better efficient of both metals removal using continuous system, which is in good agreement with the simulation results. Further research should focus on the factors influencing the efficiency and the mechanism of removal.

4. Conclusions

The optimized geometries for both batch and continuous system reactor were simulated, results show that the tuner length of 70 mm, reactor radius and height with 20 mm and 40 mm respectively; high metal removal rate can be achieved with the optimized reactor, however results also show that the temperature distribution was not uniform.

In order to improve the temperature uniformity, a continuous system was simulated. It was found that different flow rate resulted in various steady temperature. Experimental results showed a Ni and V removal rate of 76.8 % and 83.2 % with a resident time of 5 min, whereas using the batch system, only 72.4 % and 76.8 % were obtained respectively for Ni and V at the same conditions.

Although the changes of material properties with heating and reaction were not considered, which would create difference between simulation and experimental results, this simulation work also gave reasonable trend in accordance with experiments and visualized understanding about microwave heating process of HDM.

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