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EFFICIENT FILTRATION SYSTEM FOR PARAFFIN-CATALYST SLURRY SEPARATION

The filtration efficiency for separating liquid paraffin (or water) from a slurry consisting of 25 wt.% spherical alumina in a Slurry Bubble Column Reactor (SBCR) comprised of a cylindrical tube of 10 cm diameter and 150 cm length was studied. Various differential pressures (ΔP) were applied to two separate tubular sintered metal stainless steel filter elements with nominal pore size of 4 and 16 μm. The experimental results disclosed that the rate of filtration increased on applying higher differential pressure to the filter element, albeit this phenomenon is limited to moderate ΔPs and for ΔP more than 1 bar is neither harmful nor helpful. The highest filtration rates at ΔPs higher than 1 bar were 170 and 248 ml/min for 4 and 16 μm, respectively. Using water as the liquid in slurry, the rate of filtration was enhanced fourfold, which clearly reveals the impact of viscosity on filtration efficiency. In all situations, the total amount of particles present in the filtrate part never exceeded a few parts per million (ppm). The statistical analysis of the SEM images of the filtrate indicated that by applying higher pressure difference to the filter element the frequency percent of larger particle size increases. The operation of filter cake removing was performed with backflashing of 300 ml of clean liquid with pressures of 3-5 bar of N_2 gas.

Keywords: Fischer-Tropsch synthesis, wax-catalyst slurry separation, slurry bubble column reactor, cake filtration, solid-liquid separation, sintered metal.

Fischer-Tropsch Synthesis (FTS) is the process of converting hydrogen and carbon monoxide (Syngas) into hydrocarbons, chemicals and fuels. This process is the heart of a GTL (Gas to Liquid) process. Two main types of reactors are main choices for a GTL, namely fixed-bed or multi-tubular, *versus* Slurry Bubble Column Reactor (SBCR). Each of them has their inherent advantages and disadvantages and selection of the best reactor for a process depends on many operational and economical parameters. Generally, the GTL process for cobalt based catalyst is carried out in a SBCR in which the fine catalyst powder is suspended in the wax by rising synthetic gas bubbles. In these reactors, gas flow of feed moves up through the slurry bed of catalysts and liquid wax, and during its travel different phenomena take place, such as diffusion and convective mass transfer and chemical reaction over catalyst surface. The final result of all of these phenomena is the conversion of Syngas to a wide range of hydrocarbons. These products are divided into two main cuts, namely the lighter cut (which is non-condensable at room temperature and pressure conditions) and the wax or heavier cut (which is condensable and hence in liquid state at room conditions). The lighter cut can be separated from the slurry by virtue of its phase difference, but liquid wax which is completely miscible with the slurry lads to some operational difficulties in separation. Hence, despite of all the advantages of a SBCR over a multi-tubular fixed bed reactor (such as lower construction cost, lower gas compression cost due to less pressure drop across reactor, relatively uniform catalyst distribution, isothermal temperature profile, relatively reduced catalyst consumption and ease of online removal or addition of catalyst), this issue should be considered and all of its problems must be solved by

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an economical and industrially feasible method. Other difficulties that also arise with SBCR include problems with scale-up due to complex interaction among phases, and catalyst attrition [1-7].

However, SBCR is still a suitable and economical choice that is favored over multi-tubular reactors in many aspects, hence investigations in different areas are continued. Nowadays with the high price of crude oil, the importance of processes that are able to produce synthetic fuels has grown rapidly. So it is of considerable importance to solve all operational bottlenecks of those types of processes, such as catalyst, hydrodynamics of reactor flow regimes, thermodynamics of separation units, etc. One of the main difficulties in application of cobalt catalyst in SBCR for FTS is the separation of solid catalyst from the liquid products present in the slurry phase. Also, the final liquid product should not exceed more than a few ppm of catalyst particles.

After more than 5 years of research in the field of separating catalyst from GTL wax in RIPI, it was proven that internal filtration is the most efficient technique from an economic and environmental point of view [7]. This issue was also confirmed by other investigations [8-9]. There are various ways to separate liquid from suspended solids, such as sedimentation, use of magnetic fields in a separator, application of centrifugal methods in hydroclone separators, etc. [9]. Each of these techniques has their natural advantages and disadvantages. Sometimes a combination of these methods may also be utilized. For example, when it is needed to reduce the solid content of a 25 wt.% slurry to less than ppm, a situation which arises in actual GTL plants, it is possible to use a sedimentation unit first to reduce the high solid content to about 2-3 wt.% followed by a filtration or magnetic separator. Although such occasions are possible, but filtration techniques still retain their importance because of benefits such as ease of design and operation, huge amount of experience and high efficiency. It should be noted that there are many parameters that affect the final behavior of a filtration system, such as the operating differential pressure, viscosity of the liquid, type of the filter media and its pore size, concentration of the solid in the slurry, physical properties of the filter cake, etc. Among all of them, the pressure difference is one of the most important parameters, since for a special filtration system and after design of that; it is not possible to change any of these variables, unless the pressure drop. Two main concepts for exploitation of filtration method to wax/ /slurry separation in a GTL plant might be applied: internal *versus* external filtration. In external filtration, the slurry should be routed to the filtration system, which is located out of the reactor. In the filtration vessel, part of the wax is separated from the slurry; hence the remaining slurry is more concentrated from solid powder. So there is a permanent need for transporting the slurry from the reactor to this system and also returning the concentrated slurry to the reactor. Remembering all problems associated with transferring a slurry phase in a pipeline, and also pumping such material, this method leads to high operational and maintenance costs. On the other hand, internal filtration is another choice that is easier in operation and can compete with the external concept in many of aspects. In this method, filter elements placed inside the reactor and connected to a filtrate product drum. By controlling the pressure of the filtrate vessel, it possible to maintain a constant pressure drop across the filter element to ensure the filtration occurrence. In this method, an efficient concept for removing the filter cake should also be considered.

In this study, the effectiveness of an internal filtration system that has been developed for separation of paraffin from suspended spherical alumina is investigated. This mixture is suitably selected to resemble the actual suspension of wax and catalysts, which is utilized in the industrial plants. The main objective of the present filtration trials is to find the effects of variations of pressure differential across the filter element on the rate and quality of filtrate. The next objective is to evaluate the effectiveness of liquid back-flashing operations to remove filter cake from the filter element.

EXPERIMENTAL SETUP

The experiments were carried out in a setup schematically shown in Figure 1. The main reactor is a stainless steel cylinder of 150 cm length and 10 cm internal diameter with two flanges at the top and middle to load or remove the catalyst. The filter elements are two stainless steel sintered metal cylinders with 4 cm outer diameter and 10 cm length with nominal pore size of 4 and 16 μm.

The filter element was fixed half way from the top of the main tube. The level of slurry in the reactor is detected with a digital electronic level meter. The 4--20 mA output of the digital level meter controls a solenoid valve that permits the flow of liquids from the main tube through the filter element into the liquid collecting vessel.

At the bottom of the main tube there exists an inlet sparger for entering gases to the reactor. The N_2 gas was injected to the vessel to generate a three-

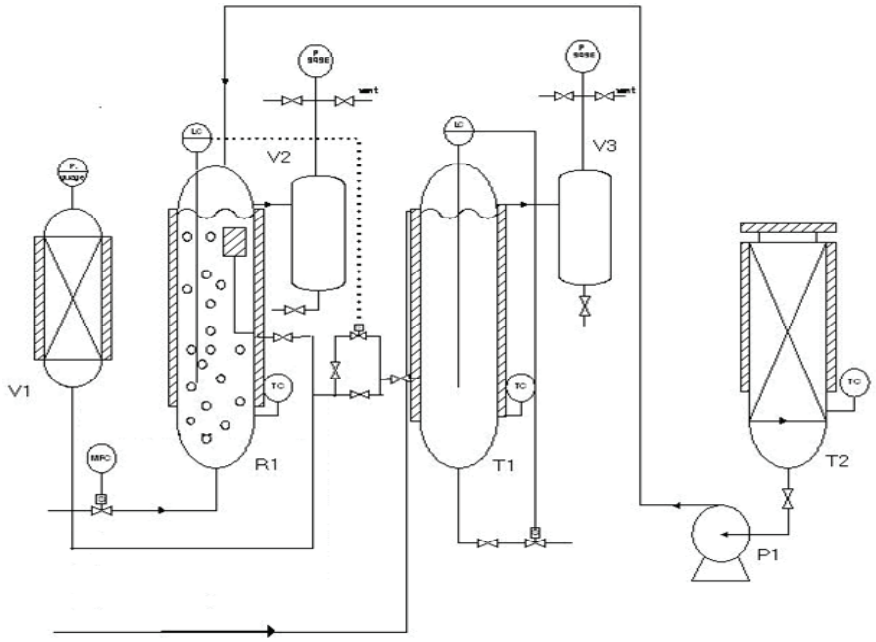

Figure 1. Schematic of the filtration test setup. R1 is the main vessel containing the slurry, T1 is the vessel for collecting the filtrate, T2 is a vessel containing clean refinery paraffin, P1 is liquid transfer pump, V1 is back-pulse tank, V2 and V3 are two knock out drums.

phase slurry in the main reactor and maintain a pressure gradient at the filter element. The pressure of the reactor was measured with a digital pressure indicator with an accuracy of 0.1 bar. The total pressure of the main tube and filtrate collecting vessel of the filtration system was controlled with backpressure valves. External heater jackets fixed on the outer walls of vessels (feed, main and filtrate vessel) were used to raise the temperature when it was necessary. The slurry consisting of a mixture of Al_2O_3 and liquid paraffin was loaded into the filtration system in which the alumina content was 25% by weight with particle size ranging from 15-100 μm. Figure 2 shows an SEM micrograph of such material. Although it seems that this sample is not completely spherical, since it is not long such as a rod or flat, it was assumed to be spherical. Also, its shape obeys the shape of a real sphere by acceptable accuracy. Refinery paraffin was selected as the liquid phase of slurry, since its viscosity at 70 °C was very close to the FT wax at about 220 °C. To have an assessment of the extent of amount of particles in the filtrate, 1-2 L of filtrate liquid was passed through a filter paper that collects particles down to 0.07 μm. The filter paper before and after filtration was dried and weighed, the difference in weight of filter paper was recorded as the measure of the amount of particles in the filtrate part.

The backflash system consists of a high-pressure piston pump, which delivers clean liquid from the filtrate container at a constant rate of 100 ml/min to a 900 ml vessel. The backflash vessel has an entrance for N_2 gas. In order to remove the solid cake developed at the surface of filter element, the pressurized liquid from the backflash vessel is suddenly sent to the filter element chamber. The high pressure flow of the backflash, which is applied at once, urges the filter cake to be removed from the filter element surface.

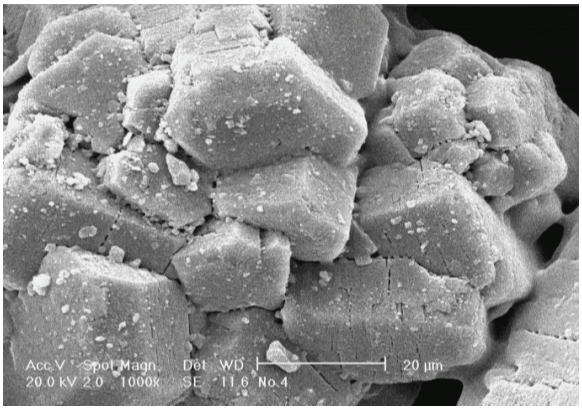

Figure 2. Scanning electron microscope (SEM) micrograph of a typical spherical alumina particle.

One of the main targets of this investigation is to study effect of pressure difference on the filtration efficiency. Various pressures differential can be applied to the filter element by adjusting the pressure of main cylindrical tube and filtrate collecting vessel. The pressure of the main tube is fixed by setting the backpressure valves installed on the output vent line.

RESULTS AND DISCUSSION

Differential pressure effect on the filtrate rate, 16 μm pore size of filter and wax

Figure 3 represents the rate of filtrate at various differential pressures applied between the main vessel containing the filter element and filtrate collecting vessel at 25 °C. The pressure differential across the filter element was varied from 0.1 to 1.5 bar. It is clear from Figure 3 that by increasing the pressure differential across the filter element, the rate of filtrate production increases. For each set of pressure differential due to the formation of the filter cake around the filter element, the rate of filtrate reduces to lower values with time. The rate of filtrate decreases more rapidly with time at higher levels of ΔP, indicating that the formation of filter cake is more rigorous at higher pressure difference across the filter.

The highest filtrate rate was 248 ml/min at 1.5 bar, which reduced to 60 ml/min in nearly 75 min. The lowest rate of filtration, which took place at ΔP of 0.1 bar with a clean filter element, was 158 which dropped to 58 ml/min in 180 min.

Keeping the physical conditions of slurry and filtering system unchanged at this stage, a tubular sintered metal filter media with nominal pore size of 4 μm was replaced with the previous filter media. Figure 4 shows the filtration rate of this filter media when the pressure differential across the filter element increases from 0.4 to 2 bar at 25 °C. The rate of filtrate increases with applying higher pressure difference to the filter media, and at the same time shows lower levels of filtrate rate when compared with the filter media of 16 μm pore size. The highest filtrate rate was 170 ml/min at a 2 bar pressure differential, which reduced to 34 ml/min over a period of 80 min. Figure 3 also indi-

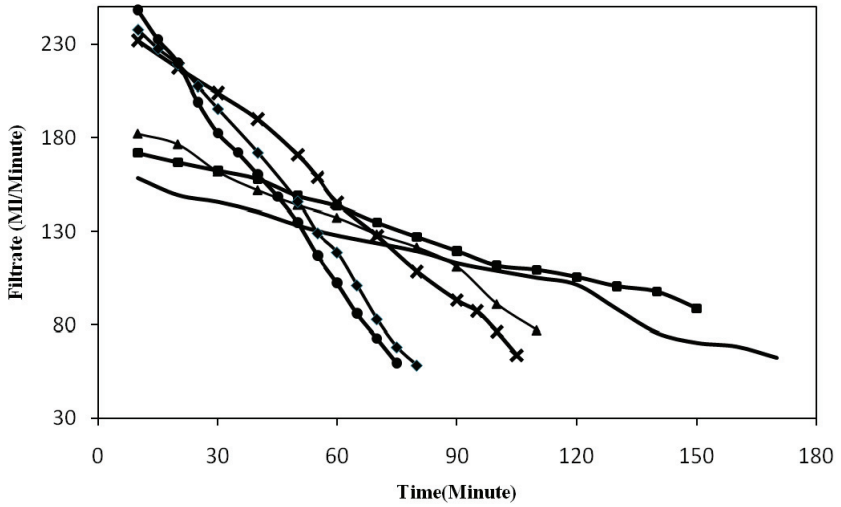

Figure 3. Solid line: ΔP = 0.1 bar, ■: ΔP = 0.2 bar, ▲: ΔP = 0.3 bar, ×: ΔP = 0.5 bar, ♦: ΔP = 1.0 bar, ●: ΔP = 1.5 bar.

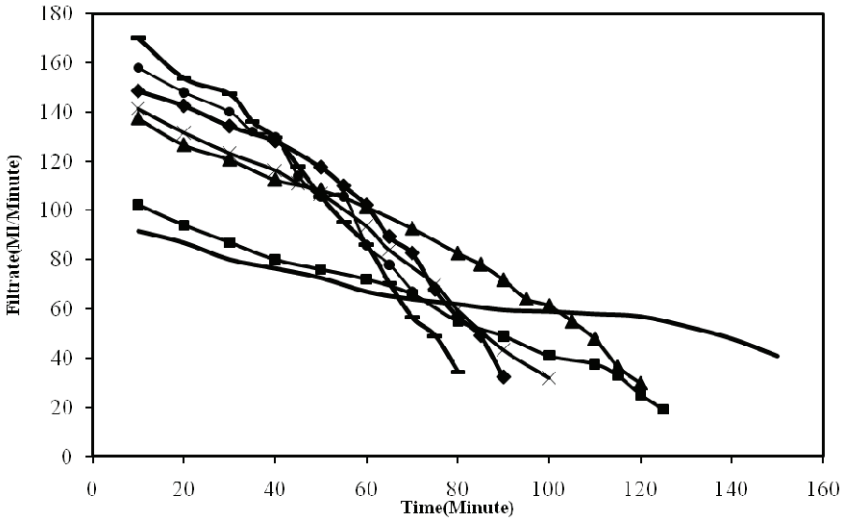

Figure 4. Solid line: ΔP = 0.4 bar, ■: ΔP = 0.6 bar, ▲: ΔP = 0.8 bar, ×: ΔP = 1.0 bar, ♦: ΔP = 1.0 bar, ●: ΔP = 1.8 bar, -: ΔP = 2.0.

cated that the rate of filtrate diminished to lower values more rigorously at higher ΔP applied to the filter media. This means that at higher ΔP across the filter media, the growth of filter cake is accelerated.

Effect of water as the liquid of slurry

To investigate the effect of changing the main component of the three-phase slurry on the rate of filtrate, slurry containing water and 25% (by weight) of spherical alumina was loaded to the reactor vessel while keeping the temperature at 25 °C. Figure 5 shows the general characteristics of the filter element with nominal pore size of 4 μm. Due to lower viscosity of water compared to refinery paraffin, the rate of clean liquid at equivalent pressure difference applied to the filter element was enhanced considerably. For example, at pressure difference of 0.4 bar, the mean rate of filtrate for the first 10 min of filtration cycle for refinery paraffin as the slurry was 91.5 ml/min (Figure 3). When the water was the main component, the rate of filtration for the same filter element was 421 ml/min (Figure 5), *i.e.*, the rate of filtrate increased more than fourfold.

Effect of differential pressure on the quality of filtrate

Figure 6 is a high resolution SEM micrograph, taken from the filtrate part, of an alumina particle that was produced in the refinery paraffin slurry due to attrition in the slurry. Although the primary alumina is spherical, because these fine powders are results of catalyst attrition their shape is not really spherical. From the SEM micrographs of the samples (Figure 5), it was found that there were no large grains passed through the filter paper.

It is clear from the micrograph that the size of the particle is less than 4 μm. The tiny particles available in the primary alumina feed are one of the sources of contaminating the final wax product synthesized in the commercial FT process. The other source of breakdown of catalyst comes from attrition of catal-

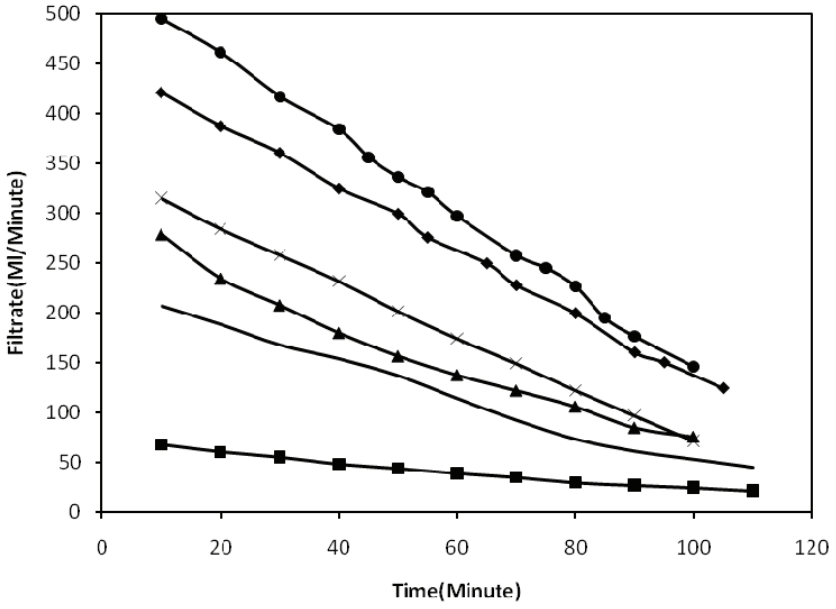

Figure 5. ■: Hydrostatic, solid line: ΔP = 0.1 bar, ▲: ΔP = 0.2 bar, ×: ΔP = 0.3 bar, ♦: ΔP = 0.4 bar, ●: ΔP = 1.0 bar.

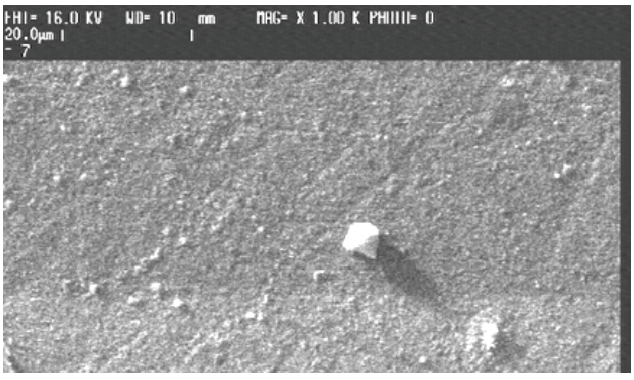

Figure 6. A typical sample of fines in filtrate product.

yst due to severe conditions of high temperature and pressure inside the reactor [8]. The tiny particles are very hard to filter and are the main source of filter clogging.

The concentration of particles suspended in the filtrate part of the slurry at a pressure differential of 0.2 bar, in time interval of 10-20 min from the beginning of the filtration process, was 1.4 ppm. Taking the same procedure at pressure differentials of 0.3 and 0.4 bars, the particle content increased to 1.6 and 1.7 ppm, respectively.

Figure 7 is the histogram of the particles size distribution passed from the filter element with nominal pore size of 16 μm at various pressure differences. The particles in the filtrate part were counted by SEM image techniques, at various differentials applied across the sinter metal filter. A glance at these figures disclosed that at higher pressure across the filter element, the number of particles with larger size tends to escape from the slurry and enter the filtrate part of the system. As it is seen from Figure 7, the frequency percent of particles larger than 20 μm is about 2 at differential pressure of 0.2 bar, while it is raised to 18 for a differential pressure of 0.6 bar applied over the same filter element.

Filter cake removing

Figure 8 shows nearly 100% of filter element efficiency is recovered in each cycle of backflushing, which was carried out with 300 ml clean liquid under 4 bar of N_2 gas. The operation of removing the cake from the filter element is carried out when the efficiency of the filter drops to about 35% of its initial value of filtration cycle.

CONCLUSION

In this study, a series of experiments have been done to find the effect of different pressure differences on the rate and efficiency of filtration operation. It was found that ascending ΔP leads to higher filtrate

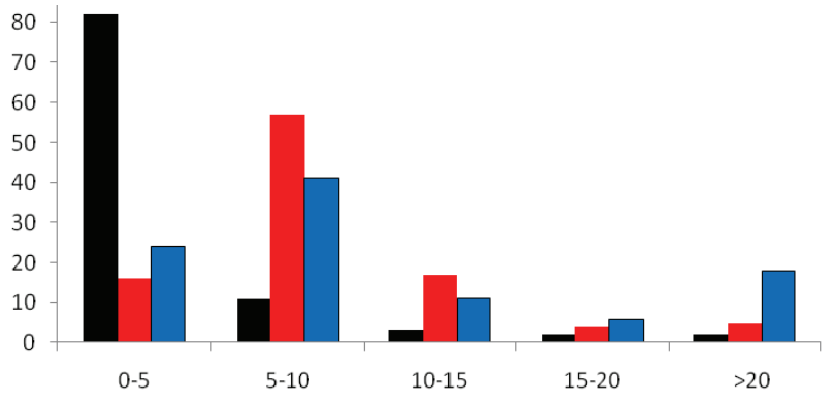

Figure 7. The Histogram of particles presented in the filtrate part of the slurry, black: ΔP = 0.1 bar, red: ΔP = 0.4 bar, black: ΔP = 0.6 bar.

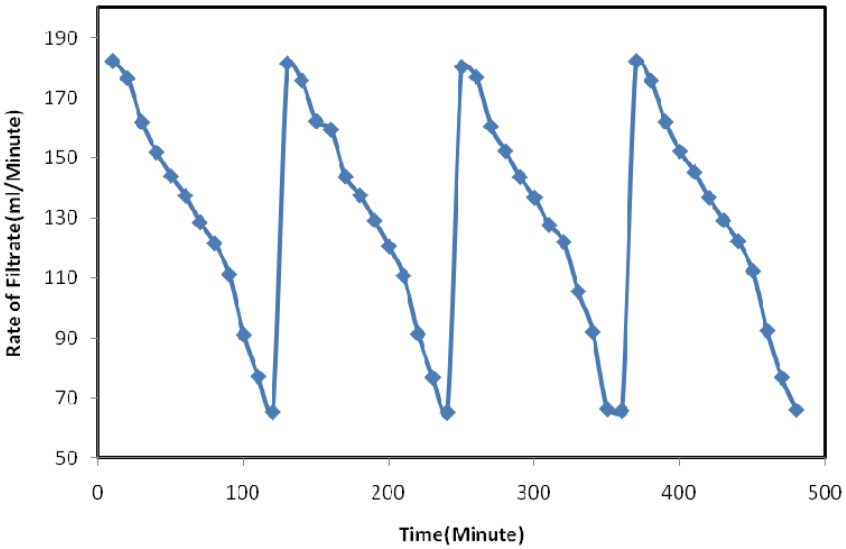

Figure 8. Back washing cycles for removing filter cake from the filter element, backflushing volume 300 ml at 4 bar.

production rate. But this effect is marginal and for ΔPs more than 1.5-2 bar, diminishes. Because the largest pore of the filter media is larger than the size of the smallest powder grain available in the product, it is possible to see a few ppm of fines in the final product. This phenomenon was exaggerated by applying higher ΔPs.

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NAUČNI RAD

EFIKASAN SISTEM FILTRACIJE ZA RAZDVAJANJE SUSPENZIJE PARAFFIN-KATALIZATOR

Proučavana je efikasnost filtracije za izdvajanje tečnog parafina (ili vode) iz suspenzije sferne alumina (25 %) u barbotažnoj koloni koja se sastoji od cevi prečnika 10 cm i dužine 150 cm. Različit diferencijalni pritisak (ΔP) je primenjen na dva odvojena cevna sinterovana filtera od nerđajućeg čelika sa nominalnim prečnikom otvora 4 i 16 μm. Ispitivanje je pokazalo da se brzina filtracije povećava sa povećanjem diferencijalnog pritiska kroz filter, iako je ovaj fenomen ograničen na umerene razlike pritiska, kao i da za ΔP > 1 bar on nije niti štetan, niti koristan. Njaveće brzine filtracije pri ΔP > 1 bar su bile 170 and 248 ml/min za otvore 4 i 16 μm, redom. U slučaju vodene suspenzije, brzina filtracije se povećava četvorostruko, što jasno ukazuje na uticaj viskoziteta na efikasnost filtracije. U svim eksperimentima, ukupna količina čestica u filtrate nije bila veća od nekoliko ppm. Statistička analiza SEM snimaka filtrate je ukazala da se primenom većeg diferencijalnog pritiska povećava učestalost pojave većih čestica. Ispiranje filtracione pogače je vršeno u suprotnom smeru sa 300 ml čiste vode pod pritiskom azota od 3-5 bar.

Ključne reči: Fischer-Tropsch-ova sinteza, sepracija suspenzija vosak-katalizator, slurry barbotažna kolona, filtracija, separacija čvrst-tečno, sinterovani metal.