The Use of Taguchi Method to Determine Factors affecting the size of fine attapulgite particles generated by Rapid Expansion of Supercritical Solution with and without cosolvents

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Abstract

The rapid expansion of a supercritical solution (RESS) process is a promising method for the production of small, uniform and solvent-free particles of solutes. The RESS containing a non-volatile solute leads to loss of solvent power by the fast expansion of the supercritical solution through an adequate nozzle, which can cause solute precipitation. The nozzle configuration plays an important role in RESS method and has a great effect on the size and morphology of the precipitated attapulgite particles. In this work, a RESS apparatus was set up and attapulgite submicron particles were prepared successfully with the supercritical carbon dioxide. The experiments were carried out to investigate the effect of parameters such as extraction temperature (308-328K), extraction pressure (150-200 bar), spraying distance (1-5 cm) ,the nozzle configuration besides the presence of cosolvents . Taguchi method creates an orthogonal array to accommodate these requirements. The selection of a suitable orthogonal array depends on the number of control factors and their levels. In this work our experiments carried out based on L18 orthogonal array. For the Taguchi design and subsequent analysis, the software named as Qualitek-4 (version 4.82.0) was used. The RESS process could produce ultrafine spherical particles (0.09 to 2.1 μm) of attapulgite as reflected by SEM observations. However the average size of the unprocessed particles were (1-100 μm) with average of 15 μm.

1 Introduction

There are a large number of clay minerals, but those with which we are concerned in drilling fluids can be categorized into three types. The first type is needle-shaped, non-swelling clays like attapulgite or sepiolite. Attapulgus clay is usually called attapulgite which comprises 80% to 90% of the commercial product. Attapulgite has a fibrous texture. It is used in drilling mud solely for its suspending qualities. The natural fine crystal size and needle shape causes it to build a "brush heap" structure in suspension and thereby exhibit high colloidal stability even in the presence of high electrolyte concentration. Attapulgite, a naturally occurring mineral, is a crystalline hydrated magnesium alumino-silicate with a three dimensional chain structure that gives it unique colloidal and sorptive properties. Attapulgite is primary among the fuller's earth family of minerals. It was first mined in Quincy, Florida in 1893. American attapulgite is only found in southwestern Georgia and northern Florida. Attapulgite's performance is enhanced by specific thermal activation and particle size control. It is used as a viscosifier in saltwater drilling fluids where bentonite becomes ineffective [1-2]. In process industries, for a variety of operations the particle size is a critical parameter. This is because finer and larger particles have different rates of settling in a liquid medium, and the difference is accentuated if the liquid medium is denser. Smaller particles have a higher total surface area for a given particle loading. This indicates that the strength increases with increasing surface area. . It is obvious that the submicron processed attapulgite improves the rheological properties which lead to reduce the operating cost of drilling. In other words, the processed attapulgite particles can better absorb water molecules due to increasing surface area and result in better suspension solution which leads to improve the performance of drilling mud. Drilling fluid properties can be extremely sensitive to the presence of slimes (ultrafine particles) which increase the viscosity of the slurry [3-4].The technology for producing fine particles with narrow particle size distribution (PSD) is one of the most crucial technologies in several fields such as material, pharmaceutical, food, polymer, and fine chemical industries. Conventional techniques for particle size reduction include mechanical comminuting (crushing, grinding, and milling), recrystallization of the solute particles from solution by using liquid anti-solvents, freeze-drying and spray-drying. Although the mechanical method is simple and economical, it is not suitable for thermally labile compounds or materials hard to crush. The other processes have a problem leading to the environmental pollution due to excessive use and disposal of solvent[5]. Supercritical fluid technology has been widely used for various applications such as extraction, reaction, chromatography and material processing**.** Carbon dioxide is the most widely used supercritical fluid, because it has a relatively low critical temperature (31.2 ^{o}C) and a moderate critical pressure (73.8 bar). In addition, it is inexpensive, leaves no toxic residue, and is not flammable. As fine particle formation processes using supercritical fluids, RESS (Rapid Expansion of Supercritical Solution), SAS (Supercritical Anti-Solvent) and PGSS (Particles from Gas-Saturated Solution) have been known[6]. The rapid expansion of a supercritical solution (RESS) process is an attractive technology for the production of small, uniform and solvent-free particles. It is to be noticed that only few examples were published on application of RESS to microspheres generation. Pre-exfoliated nanoclays were prepared using supercritical carbon dioxide as solvent by several authors C. Detrembleur et al.[7]. It should mention that there are a few papers in field of clay/polymer nanocomposites in recent years were published [8]. In this work, a RESS apparatus was set up successfully and was used to produce attapulgite fine particles which can be used as a viscosifier in drilling mud. Several authors have reviewed the applications of RESS on the preparation of fine and ultra fine particles. For instance Formation of anthracene fine particles by Nagahama et al [9]. To our knowledge, no research paper is available on micronization of attapulgite by supercritical carbon dioxide. It is obvious that the submicron processed attapulgite improves the rheological properties which lead to reduce the operating cost of drilling. The experiments were carried out to investigate the effect of extraction temperature (308–328 K) and pressure (15–20MPa), spray distance (1-5 cm), nozzle diameter (500-1200 μm) and the presence of cosolvents(Isopropyl alcohol and acetone) on the size and morphology of the precipitated attapulgite particles. Precipitated attapulgite particles were analyzed their size by scanning electron microscopy (SEM) .Before the SEM analysis, the process either original samples must be coated by a sputter-coater **.** Our current research is aimed towards an improved understanding of the relationship between process parameters and particle characteristics and to explore new areas of application for nanoscale particles. Taguchi method creates an orthogonal array to accommodate these requirements. The selection of a suitable orthogonal array depends on the number of control factors and their levels. Taguchi design is preferred because it reduces the number of experiments significantly. With the selection of L18 orthogonal array, using five mentioned parameters and their levels(3 levels), the number of experiments required can be drastically reduced to 18. It means that 18 experiments with different combinations of the factors should be conducted in order to study the main effects, which in the classical combination method using full factorial experimentation would require 3^5 = 243 number of experiments to capture the influencing parameters. These control factors include Temperature, Pressure, Nozzle Diameter, Spraying Distance, and Cosolvents. All control factors have three levels. For the Taguchi design and subsequent analysis, the software named as Qualitek-4 (version 4.82.0) was used.

2 EXPERIMENTAL

2.1 Materials

The solute used during this study, attapulgite, was prepared from PDF company (Pars Drilling Fluid company,Tehran-Iran) and Carbon dioxide (99.9 %< purity) was purchased from Abughadareh Gas Chemical Company(Shiraz-Iran). The solvents, Isoporopanol (Isopropyl alcohol) and acetone was purchased from Merck.

2.2 RESS Set up

The RESS pilot plant is shown in Fig. 1,2. At first, the gaseous CO2 from a cylinder capsule was passed through a filter and then entered into a refrigerator to make liquid CO2. The liquid CO2 was then pumped by a reciprocating oil-free water-free high pressure manual pump into a vertical surge tank. The pressurized CO2 then entered into an extraction vessel (Vessel 1) which is containing with cosolvent. The attapulgite were charged with glass wool and specific packing in another extraction column (Vessel 2), and was held it in the desired conditions for two hours to ensure complete equilibrium has been obtained. The equilibrated solution was then expanded into a nozzle. The precipitated attapulgite particles were collected on the stub and analyzed by a SEM to monitor the particle size and its morphology. A new type of nozzles was designed and fabricated to achieve ultrafine nanosize particles.

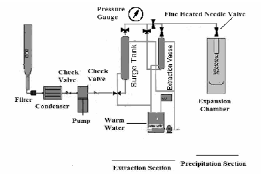


Fig.1. The schematic diagram of the experimental apparatus for the RESS process

Fig.2.The SCF apparatus was set up in Shiraz University

2.3 Particle size and morphology

The morphology and size of the precipitated attapulgite particles were examined by using scanning electron microscopy (SEM) (S360- CAMBRIDGE). In brief, prior to examine the samples by a SEM the precipitated attapulgite particles were collected on the conductive stubs which were then coated by a sputter-coater (SC-7640-Polaron) with Pd-Pt under the presence of argon (99.9% < purity) at the room temperature for a period of 100 s under an accelerating voltage of 20 KV . The mean particle size of the precipitated particles was calculated by SigmaScan Pro Image analysis.

2.4 Nozzle configuration

The structure of the new nozzle is illustrated in Fig. 3. The nozzle comprises two parts, shell part and inside part. In this design, the clearance between the inside part and the nozzle acts as a circular orifice so that supercritical fluids can spray from a narrow exit in a few microns. Also the swirled channel enhances the chance of spherical form particles formation which could be helpful to improve the particle morphology design. In the entrance of the nozzle, $SC\text{-}CO_2$ is introduced through the spiral channel, so the fluids can be swirled out of the nozzle. In this kind of nozzle instead of the usual diameter, the effective nozzle diameter has been defined.

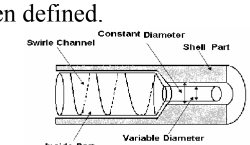
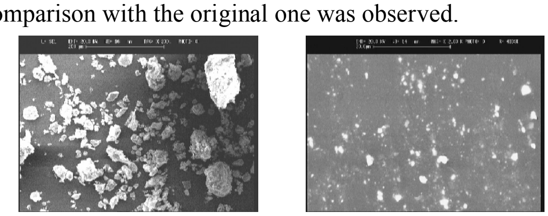


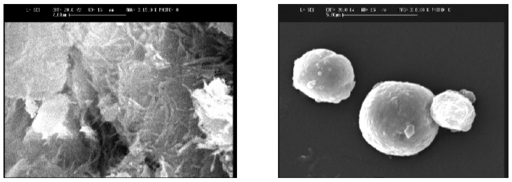
Fig.3. Schematic diagram of the used nozzle

2.5 Image analysis

As can be seen in Fig.4 the rapid expansion of supercritical solutions (RESS) was successfully used to produce attapulgite submicron particles. Attapulgite was micronized and a great size reduction of attapulgite particles in comparison with the original one was observed.



(a) (b)



(c) (d)

Fig.4.(a,c) Unprocessed Attapulgite (b,d)Precipitated Attapulgite by RESS process

3 Results and Discussion

In this work, the influence of RESS parameters such as extraction temperature (308-328 K), extraction pressure (150-200 bar), spraying distance (1-5cm) and effective nozzle diameter (500-1200 µm) and cosolvent (**-** =without cosolvent, SOL 1=Isopropanol, SOL 2=Acetone) were investigated on the mean particle size of the micronized attapulgite particles which are expressed below. In addition, the Taguchi method was used to arrange the experimental conditions of micronization of attapulgite particles based on L-18 array as shown in Table 2.

RUN	P	T	ND	SD	COSOLVENT	Average particle size(µm)
1	150	35	500	1	-	1.00
2	150	45	900	3	SOL1	0.75
3	150	55	1200	5	SOL2	1.5
4	175	35	500	3	SOL1	0.25
5	175	45	900	5	SOL2	0.65
6	175	55	1200	1	-	1.7
7	200	35	900	1	SOL2	0.09
8	200	45	1200	3	-	0.85
9	200	55	500	5	SOL1	0.55
10	150	35	1200	5	SOL1	1.25
11	150	45	500	1	SOL2	0.3
12	150	55	900	3	-	2 .1
13	175	35	900	5	-	1.45
14	175	45	1200	1	SOL1	0.17
15	175	55	500	3	SOL2	0.7
16	200	35	1200	3	SOL2	0.5
17	200	45	500	5	-	0.45
18	200	55	900	1	SOL1	0.35

Table1.L-18 Taguchi Orthogonal Array

The results of the experiments show that the presence of cosolvent is the most effective parameter in the size reduction of attapulgite particles. However the extraction pressure and extraction temperature have an important role on the size and morphology of the precipitated attapulgite particles. On the other hand, higher spraying distance and nozzle diameter cause to increase particle size distribution of the precipitated attapulgite particles. Analysis of variance (ANOVA) was used to determine the optimum conditions and most significant process parameters for the micronization of attapulgite particles. For Taguchi design the statistical software namely Qualitek-4 was applied. (fig.5.) (Dark blue=Cosolvent, Green=Pressure , Blue=Temperature , Red=Nozzle Diameter ,Violet=Spraying Distance). The results of analysis show that the optimum pressure, temperature, nozzle diameter and spraying distance and cosolvent are 200 bar, 45^0C , 500 µm, and 1 cm and with the presence of Isopropanol respectively. It has to be noticed that the impression of cosolvent is very important. Anova table is drafted below (Table2).As can be observed in Fig.6 the difference between the condition of factors and their levels in table L-18 is definitely proven. because in high temperatures the attapulgite particles are agglomerated. On the contrary by increasing the pressure the attapulgite particles become spherical (Fig.6.)

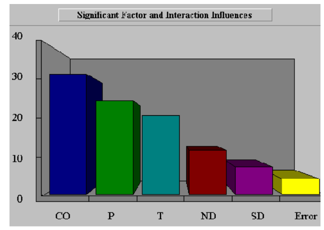
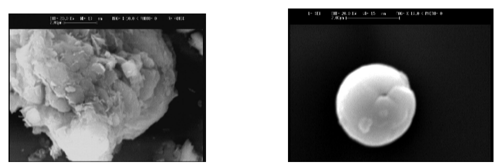


Fig.5. Significant Factor Influences for precipitated attapulgite particles

FAC	DOF	Sum of Sqrs	Var iance	F-Ratio	Pure Sum	(%)
P	2	1.0408	0.704	52.464	1.381	**24.57**
T	2	1.186	0.593	44.206	1.159	**20.63**
ND	2	0.684	0.342	25.486	0.657	**11.69**
SD	2	0.437	0.218	16.307	0.41	**7.30**
CO	2	1.81	0.905	67.439	1.783	**31.72**
Other/ Error	7	0.093	0.013			**4.06**
Total	17	5.621				**100%**

Table2. Anova Table for L-18 attapulgite



(a)L-18#12 (b) L-18#17

Fif.6.The SEM images of attapulgite (#12&#17 L-18)

3.1 Effect of Cosolvent (CO)

Attapulgite solubility is low in SC-CO2, because CO2 is a nonpolar compound. Therefore, a polar co-solvent such as Isopropylalcohol and acetone can be used together with CO2, to increase the solvating power of CO2. Increasing co-solvent concentration caused a change of morphology of the attapulgite particles. Similar result has been reported by N. Yildiz et al [10]. In other words the average particle size of attapulgite is decreased in the presence of cosolvent. However the type of solvent which is used as a cosolvent is related to the chemistry of solute. In this research because of structure of attapulgite Isopropylalcohol as a polar protic solvent is most effective. Acetone as a polar aprotic solvent is useful as well.

3.2 Effect of Extraction Pressure (P)

The extraction pressure was studied from 15 to 20MPa. The solubility of solid in supercritical fluid can be suddenly changed by slight shift of pressure, which can cause the variation of the characteristics of recrystallized particles due to a direct effect on supersaturation**.** As results show the micronization of attapulgite particles is too sensitive to a slight increase of pressure. The reason for this is that with increasing the pressure, the solubility of attapulgite particles increases sharply. In fact, an increase in the solute solubility results in higher supersaturations in the fluid upon expansion. According to the classical theory of nucleation, higher supersaturation causes higher nucleation rate and the particle volume is inversely proportional to the nucleation rate, our above results appear to agree with simple theoretical predictions**.** Similar results were reported by A.Z. Hezave and other authors [11-12].

3.3 Effect of extraction temperature (T)

The extraction temperature for attapulgite in this study ranges from 35 to 55 $^{\circ}$C. Increasing the extraction temperature leads to a decrease in the density of CO2 and a concurrent increase in the solute's sublimation pressure. The decrease of the solvent density causes a decrease of the solvent strength. On the other hand, a concurrent increase in the solute's vapor pressure is responsible for an increase in the aspirin solubility. The net effect of these two competing factors results in an increase in the saturated attapulgite concentration in the supercritical fluid [13]. Therefore, high extraction temperature induces high attapulgite solubility (i.e., high solute concentration) at a constant extraction pressure. At lower extraction temperature, the supersaturation and nucleation rate are lower since attapulgite concentration is lower. Thus crystals initialized during the expansion might preferably grow to become larger and possibly produce one-dimensional (i.e., needle-shaped) particles along the flow direction under the shear forces. However, continuously increasing temperature (at 55^0C) caused to increase of the average particle size. Because increasing the temperature leads to increase the attapulgite concentration. During the expansion, high attapulgite concentration brings about the increase of the particle size, as a consequence of coagulation among particles.

3.4 Effect of nozzle diameter (ND)

It was expected that the nozzle diameter and its dimension in the RESS process affected the particle formation. In this study, the effect of the effective nozzle diameter was investigated (500-1200 µm) on the size and morphology of the precipitated attapulgite particles. Cleary, the average particles size reduces by decreasing the nozzle diameter. In other words, the particle size increases and the PSD becomes broad with increasing nozzle diameter (nozzle1=500, nozzle2=900, nozzle3=1200). Same result was reported by Wang et al[12].

3.5 Effect of spraying distance (SD)

The spraying distance can have a pronounced effect on the characterization of the attapulgite particles, since the nucleation and growth process continues in post-expansion region [14]. In this study, three spraying distances (1, 3,5cm) from the tip of the nozzle were tested. The results show only a little change in the spraying distance from 1 cm to 5cm causes to increase the average particle size. Similar results were reported by Yildiz et al[10].

4 Conclusion

The rapid expansion of supercritical solutions (RESS) was successfully used to produce attapulgite submicron particles. Attapulgite was micronized and a great size reduction of attapulgite particles in comparison with the original one was observed. The precipitated particles of attapulgite were in the range of 10 nm to 5 µm. The obtained results shows a good performance of these used nozzles in comparison with the capillary nozzle.We conclude that presence of cosolvent is an essential factor for micronization of solute in RESS process with SC-CO2 due to the Carbon dioxide's weak solubility power . The extraction pressure and temperature also play main role in the precipitated attapulgite particle size and its morphology. In addition, the optimum Pressure, Temperature, Nozzle Diameter, Spraying Distance and Cosolvent for micronization of attapulgite particles are 200 bar, 318 K , 500 µm , 1 cm with the presence of Isopropanol respectively.

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