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Increasing the conversion fraction of sulfur to sodium thiosulfate with the ultrasound energy

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Abstract−The usage of ultrasound has gained popularity in the recent years. Ultrasonic processing means blasting liquids, usually water, with very intense sound at high frequency, producing very well mixed powerful chemical and physical reactions. This paper deals with the investigation of the effect of ultrasonic energy on the conversion fraction of sulfur in the production reaction of sodium thiosulfate which was obtained from sulfur and Na_2SO_3 solution. Concentration of Na_2SO_3 solution parameter was chosen as the constant parameter. The experiments were performed with various amplitudes of ultrasound power and in the absence and presence of ultrasound energy in various temperatures with various particle sizes. The results indicate that the conversion fraction values increase in the presence of ultrasound energy and increase at high amplitude values.

Key words: Effect of Ultrasound, Sodium Thiosulfate, Cavitation, Ultrasound Energy

INTRODUCTION

Sodium thiosulfate is also called sodium hyposulfite or hypo. Sodium thiosulfate is a source of the thiosulfate ion ($S_2O_3^{-2}$) which is very effective in complex silver ions. It is also a reducing agent of moderate strength. Sodium thiosulfate is most commonly used as a fixing agent for films and prints in the photography industry. The other application areas of sodium thiosulfate include dechlorination of water and waste water, dechlorination in textiles and pulp and paper, flue gas purification, leather tanning, graphite lubricant additive, soaps and shampoos [Iliev et al., 2000; Inoue et al., 2000]. Sodium thiosulfate is typically manufactured by reacting sodium sulfite with sulfur as represented in the following chemical equation:

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

For this equation ultrasound energy is used to increase the conversion fraction of sulfur. The studies in recent years have indicated that ultrasound energy accelerates the dissolution of ores. It is known that ultrasound may have a number of beneficial effects on chemical reactivity, such as increasing the surface area between the reactants, accelerating dissolution, renewing the surface of a solid reactant or catalyst. It has been recognized for many years that ultrasound energy has great potential for uses in a wide variety of processes in the chemical and allied industries. Applications include cleaning, sterilization, flotation, drying, degassing, defoaming, soldering, plastic welding, drilling, filtration, homogenization, emulsification, dissolution, deaggregation of powder, biological cell disruption, extraction, crystallization and a stimulus for chemical reactions [Mason and Lorimer, 1989; Mason, 1990].

Like any sound wave, ultrasound is transmitted via waves which alternately compress and stretch the molecular structure of the medium through which it passes. Thus the average distance between the molecules in a liquid will vary as the molecules oscillate about their mean position. If a sufficiently large negative pressure is applied to the liquid that the distance between the molecules exceeds the critical molecular distance necessary to hold the liquid intact, the liquid will break down and voids will be created as cavitation bubbles will form. In succeeding compression cycles these cavities can collapse violently with the release of large amounts of energy in and around these micro bubbles. By using ultrasound energy these cavities are created. When these cavities collapse, the energy oscillates and they incur destruction on the solid surface [Suslick, 1994; Atchley and Crum, 1988; Ceccio and Brennen, 1991; Shah et al., 2000].

The kinetics of p-nitrophenol degradation and the effect of reaction conditions and cavitational parameters for a multiple frequency system was studied [Sivakumar et al., 2002]. Another study is the effect of ultrasound on the induction time and the metastable zone widths of potassium sulphate. It was found from the experimental results that ultrasound had an effect on the primary nucleation of potassium sulphate. Ultrasound allowed induction time and metastable zone with it to be significantly reduced [Lyczko et al., 2002].

Effect of ultrasound on sulfuric acid-catalysed hydrolysis of starch was studied. It was found that the activation energies of the control and the ultrasound-aided hydrolysis of maltose were 30.2 and 23.4 kcal/mol, respectively. Enhancement was thus expressed as the alleviation of activation energy by ultrasound irradiation [Choi and Kim, 1994]. Effects of ultrasound on synthesis of mullite by sol-gel processes were investigated. It was observed that the specific surface area of mullite powder synthesized by sonogel process was increased with ultrasonic energy density, and the crystallinity of mullite powder prepared with moderate ultrasound was much greater than that prepared from normal gel process [Woo et al., 1996].

A dissolution and reaction modeling for hydrolysis of TEOS in heterogeneous TEOS-water-HCl mixtures under ultrasound stimulation were studied [Donatti et al., 2001]. Comparison of ultrasound effects in different reactors at 20 kHz was investigated [Faid et al., 1998]. The effect of ultrasound on the dissolution kinetics of phosphate rock in HNO_3 was studied [Tekin, 2002]. The comparison of the effects of ultrasound and mechanical agitation on a reacting solid-

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liquid system was investigated [Hagenson and Doraiswamy, 1998]. It was found that ultrasound enhanced the intrinsic mass transfer coefficient as well as the effective diffusivity of the organic reactant through the ionic lattice of the product layer.

Reaction pathways and kinetic modeling for sonochemical decomposition of benzothiophene were studied [Kim et al., 2003]. The effect of ultrasonic waves on the fabrication of TiO_2 nanoparticles on a substrate using a self-assembly method was investigated [Yun et al., 2004]. It was found that ultrasonic waves were very effective in both enhancing the surface uniformity and narrowing the particle size distribution of the titania nanoparticles.

The effect of ultrasound on aluminium trihydroxide crystallization from sodium aluminate solution was studied [Zhao, 2002]. One study was the effect of ultrasound on the dissolution of colemanite in H_2SO_4 [Okur et al., 2002]. It was found that the effect of ultrasound was on the pre-exponential factor A in the Arrhenius equation. The effect of ultrasound on desorption equilibrium was studied [Qin et al., 2001]. Influence of preparation parameters on characteristics of zirconia-pillared clay using ultrasonic technique and its catalytic performance in phenol hydroxylation reaction was observed [Awate et al., 2001].

This paper deals with the investigation of the effect of ultrasonic energy on increasing the conversion fraction of elemental sulfur in Na_2SO_3 solution with various amplitudes of ultrasound power, temperatures and particle sizes.

EXPERIMENTAL

Pure elemental sulfur was used for the experiments. From the elementary analysis it was found that the elemental sulfur was 99% in purity. A schematic illustration of experimental setup is shown in Fig. 1. It contains an ultrasonic generator (Type Cole Parmer, Ultrasonic Homoginezer, 400 W, 20 kHz) together with a probe with tip radius of 1 cm and dissolution vessel equipped with a thermocouple. In a typical experiment 400 ml of Na_2SO_3 solution was poured into a thermostatic vessel, and between 0.5 and 1 g amount of elemental sulfur was added and stirred mechanically. Solution samples were taken at corresponding intervals of time filtered immediately with vacuum pump and analyzed for determining $Na_2S_2O_3$ with volumetric method [Snell and Biffen, 1944]. This volumetric method was realized in this way: 2 ml of this filtered solution was transferred a glass for preparing it to 50 ml with distillated water. Then 15 ml of 40% of formaldehyde solution and 10 ml of 1 N. concentration of acetic acid solution were added. In this way formaldehyde shaded the sulfide ions and detached them from the thiosulfate ions. To prevent the dissociation of this complex the solution was delayed in ice bath for a few minutes. After that it was titrated with 0.01 N concentration of iodine solution. 0.5% amidine solution was used as indicator. Conversion fractions of sulfur were calculated from the expended volume of iodine solution.

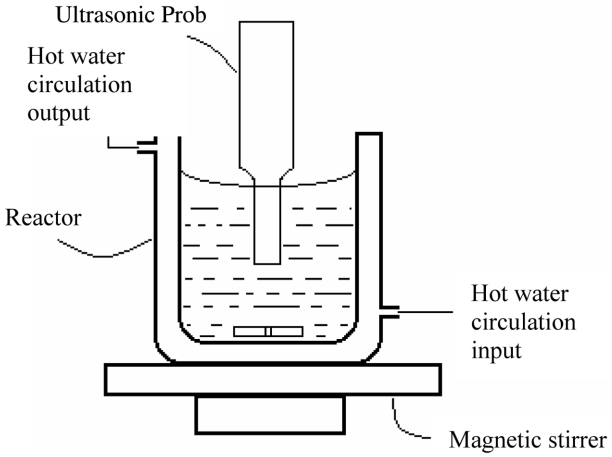

Fig. 1. Schematic of experimental apparatus for dissolution.

$$X_S = \frac{\text{Amount of sulfur in the solution}}{\text{Initial sulfur amount}}$$

$$X_S = \frac{V_{sol} \times 0.1581 \times N \times M_S \times V}{M_N \times V_F \times m}$$

Here 0.1581 is correction factor.

All the dissolution experiments were repeated in the same conditions with using the ultrasound power.

RESULTS AND DISCUSSION

In this paper −20+30 mesh particle size, 1 M concentration of Na_2SO_3 solution, 50 °C of temperature and 50% amplitude of ultrasound power were chosen as constant parameters to investigate the effect of ultrasound energy on the conversion fraction of sulfur at various temperatures, various amplitudes of ultrasound power and various particle sizes. Experiments were conducted in both the presence (ultrasound power: 26.15 W) and absence of ultrasound to ascertain the effect of ultrasound. In all the experiments, a stirring rate of 600 rpm was applied with a magnetic stirrer to avoid particles settling in the reactor. Conversion-time data obtained with various temperatures are given in Table 1, with various particle sizes given

Table 1. Percent dissolved S vs time at various temperatures

	Temperature (°C)							
	S% dissolved without ultrasound				S% dissolved with ultrasound			
Time (min)	40	50	60	70	40	50	60	70
30	0.330	0.880	0.960	1.150	4.690	5.160	7.860	14.78
60	2.170	3.850	4.920	5.880	10.83	11.67	16.73	30.69
90	2.950	5.420	6.890	7.800	14.78	16.73	30.21	46.24
120	3.450	6.770	10.27	14.47	21.16	26.08	41.82	62.02
150	4.430	8.860	13.06	17.09	27.08	35.32	55.96	76.79
180	5.350	10.81	15.84	19.32	33.49	45.17	68.32	87.03

Table 2. Percent dissolved S vs time at various particle sizes

	Particle size (mesh)							
	S% dissolved without ultrasound				S% dissolved with ultrasound			
Time (min)	−10+20	−20+30	−30+40	−40+45	−10+20	−20+30	−30+40	−40+45
30	1.600	0.880	4.110	10.78	3.440	5.160	14.64	15.80
60	2.300	3.850	8.640	13.50	7.400	11.67	29.40	36.22
90	3.500	5.420	10.75	16.51	10.33	16.73	35.70	50.21
120	4.810	6.770	11.82	18.50	15.26	26.08	37.04	63.50
150	6.330	8.860	13.77	20.73	24.27	35.32	44.07	73.69
180	7.730	10.81	14.36	26.25	37.50	45.17	62.14	82.01

Table 3. Percent dissolved S vs time at various amplitudes of ultrasound power

	Amplitude (%) S% dissolved		
Time(min)	40	50	60
30	1.59	5.16	15.31
60	6.89	11.67	37.26
90	9.27	16.73	53.67
120	18.05	26.08	69.42
150	26.37	35.32	80.25
180	28.79	45.17	87.61

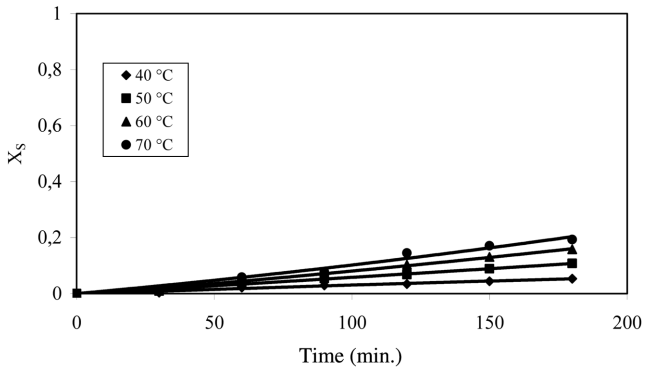

Fig. 2. Fraction of dissolved S versus time, at various temperatures in the absence of ultrasound.

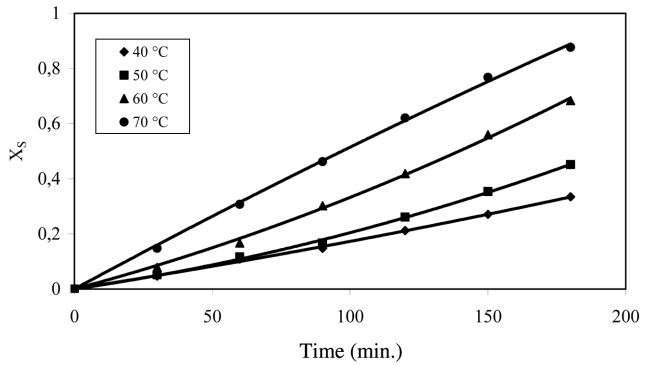

Fig. 3. Fraction of dissolved S versus time, at various temperatures in the presence of ultrasound.

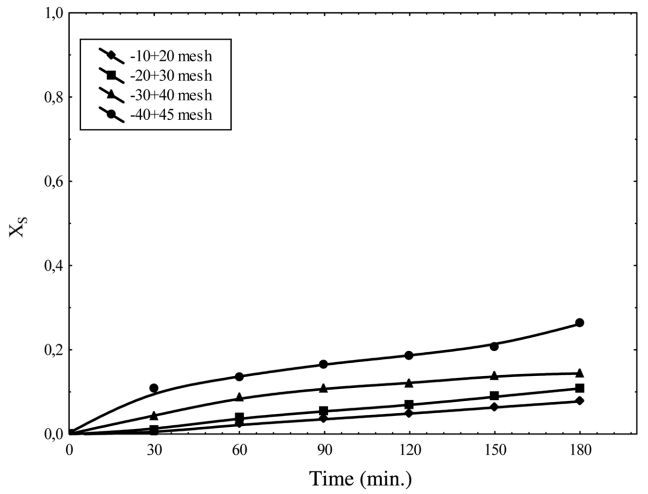

Fig. 4. Fraction of dissolved S versus time, at various particle sizes in the absence of ultrasound.

in Table 2, and with various amplitudes of ultrasound power given in Table 3. It is clearly seen that ultrasound and ultrasound power enhances the reaction rates. Also, this increase can be seen when the Fig. 2, Fig. 3, Fig. 4, Fig. 5, Fig. 6 and Fig. 7 are compared. Conversion fraction values of sulfur versus temperature are depicted in Fig. 7 while the time is constant at 150 minutes. It is seen that in the presence of the ultrasound energy the conversion fraction values are higher than the values in the absence of the ultrasound energy.

It was found that the conversion fraction values of elemental sulfur in the presence of ultrasound energy were higher than the values in the absence of ultrasound energy. And also it was remarkable that the conversion fraction values of sulfur increased with the increasing of temperature. Here are some examples of these results. In the absence of ultrasound energy a conversion value of approximately 5% was obtained in 90 minutes. In the same conditions the same conversion value was obtained in 30 minutes in the presence of ultrasound energy. In the absence of ultrasound energy a conversion value of approximately 16% was obtained in 180 minutes. In the same conditions the same conversion value was obtained in 60 minutes in the presence of ultrasound energy.

While in the 50 °C value in the absence of ultrasound energy the conversion value was 5.42%; in the same conditions and in the presence of ultrasound energy the value was 16.73%. While in the 60 °C value in the absence of ultrasound energy the conversion value was 10.27%; in the same conditions and in the presence of ultrasound

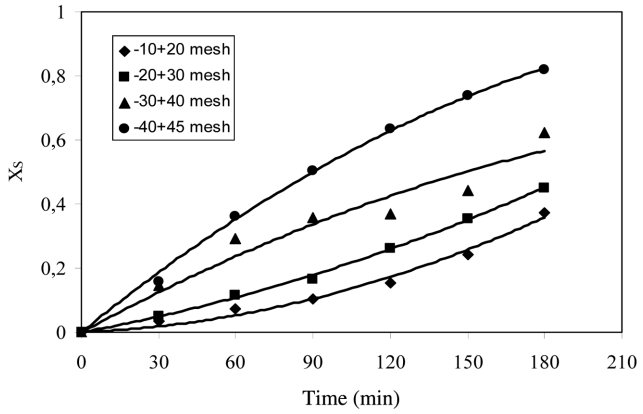

Fig. 5. Fraction of dissolved S versus time, at various particle sizes in the presence .

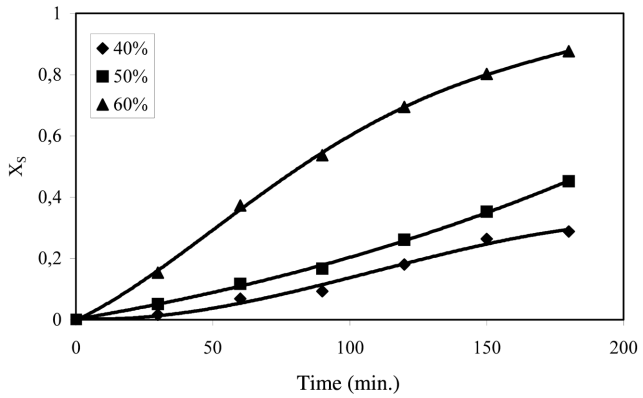

Fig. 6. Fraction of dissolved S versus time, at various amplitudes of ultrasound power.

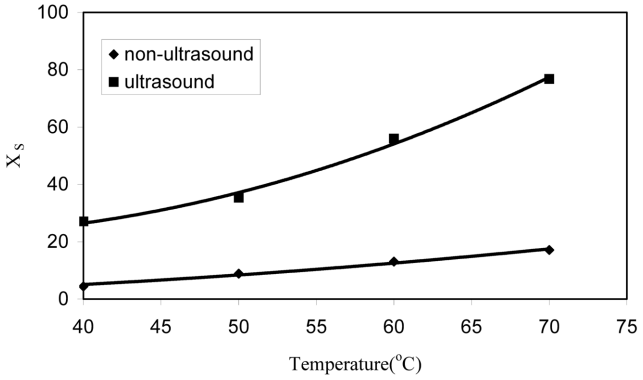

Fig. 7. Fraction of dissolved S versus temperature, at constant time (150 min) in the presence and absence of ultrasound.

energy the value was 41.82%. While in the 70 °C value in the absence of ultrasound energy the conversion value was 19.3%; in the same conditions and in the presence of ultrasound energy the value was 87.03%.

Also, it can be seen from the results that the conversion fraction values of sulfur increased with the increasing of the amplitudes of ultrasound power. For example, in 40% amplitude value the conversion value was 6.89% at 60 minutes. But in 60% amplitude value the conversion value was 37.26% at 60 minutes. And in 50% amplitude value the conversion value was 35.32% at 150 minutes, but in 60% amplitude value the conversion value was 80.25% at 150 minutes.

Smultaneously with the decreasing of the particle size the conversion fraction values of sulfur increased. For instance in −10+20 mesh particle size value in the absence of ultrasound energy the conversion value was 1.60% at 30 minutes, but in the same conditions and in the presence of ultrasound energy the conversion value was 3.44%. While in −30+40 mesh particle size value in the absence of ultrasound energy the conversion value was 14.36% at 180 minutes, but in the same conditions and in the presence of ultrasound energy the conversion value was 62.14%.

From the results, it was found that in the presence of ultrasound energy the same conversion value was gained in a shorter time.

Shock waves are created by using ultrasound energy. Cavitation occurs by the shock waves. The surrounding liquid molecules rush in to fill that cavity. When they reach the center of the cavity, they collide with each other and the solid surface with great force. This generates many micro cracks and dimples. It is known that these

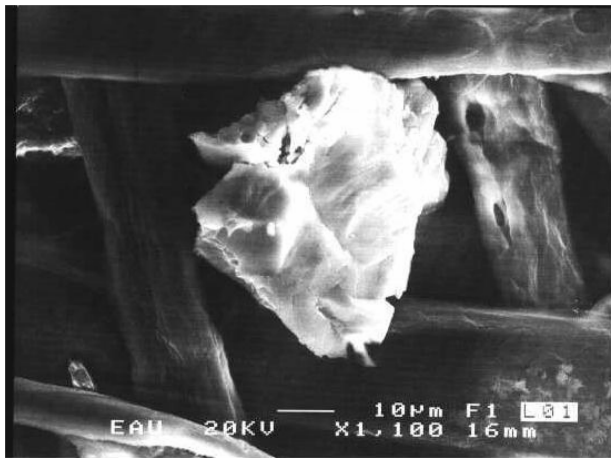

Fig. 8. The SEM photograph of sulfur in absence of ultrasound energy.

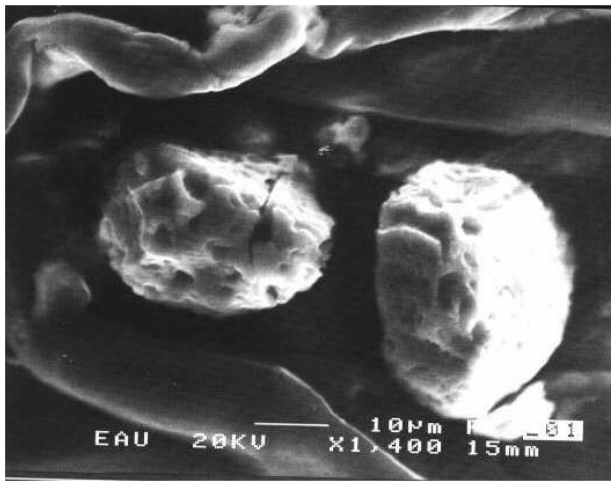

Fig. 9. The SEM photograph of sulfur in presence of ultrasound energy.

micro cracks and dimples cause a reaction or raise the reaction speed by increasing the effective area of reaction with providing a new surface. To obtain clearly the mechanical effect of ultrasound energy, two photographs of sample were taken with a scanning electron microscope (SEM) (Fig. 8 and Fig. 9) in both the absence and presence of ultrasound energy in the same conditions. It is seen from these photographs that ultrasound energy does not affect the diameter of particle. In other words there has not been any shrinking or crumbling in the particle. But some cracks and dimples are seen on the sulfur surface when the ultrasound energy is used. It is supposed that the formation of these cracks and dimples that increase the effective area of reaction are derived from ultrasound energy.

CONCLUSION

- It is obtained from the results that the conversion values increased in the presence of ultrasound energy.
- Increasing the temperature and decreasing the particle size, the conversion fraction values increase.
- Also increasing the amplitude of ultrasound energy, the conversion fraction values become higher than conversion values in the low level amplitude of the ultrasound energy.
- In addition in the presence of ultrasound energy the same conversion value is accessed in shorter time than in the absence of ultrasound energy. It is seen from the Fig. 7 that the conversion fractions of sulfur increase approximately a proportion of 78% in the presence of ultrasound energy.
-We consider that the obtained cracks and dimples increase the effective area of reaction which raises the reaction speed.

NOMENCLATURE

X_S : conversion fraction of sulfur
V_{Sol} : solution volume [400 ml]
N : normal concentration of iodine solution
M_S : molecule weight of sulfur [g/mol]
V : expended iodine solution volume [ml]
M_N : molecule weight of sodium thiosulfate [g/mol]
V_F : volume of solution which used in titration [2 ml]
m : initial sulfur amount [gram]

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