Title: Progress in Development of Ultrasonic Probe Technique for Hydrodynamic Characterization

Authors: Y. Soong, I. K. Gamwo, F. W. Harke, A. G. Blackwell, E. P. Ladner and M. F. Zarochak

SOONG@FETC.DOE.GOV (412) 892-4925 (O) (412) 892-4152 (Fax)
U.S. Department of Energy, Federal Energy Technology Center,
P.O. Box 10940, Pittsburgh, PA 15236

Abstract

An ultrasonic technique was developed to measure the slurries concentration in an autoclave reactor. Preliminary measurements were conducted on slurries consisting of molten FT-200 wax, glass beads, and nitrogen bubbles at a typical Fischer-Tropsch (FT) synthesis temperature of 265°C. The data show that the velocity and attenuation of the sound are well-defined functions of the solid and gas concentrations in the molten FT-200 wax.

Introduction

Fischer-Tropsch (FT) synthesis represents an important route to convert coal-derived synthesis gas to premium-quality fuels such as light hydrocarbon, gasoline, or diesel fuels depending on the catalyst employed, the reaction temperature, and the process employed. The slurry phase FT process is considered a potentially economic method to convert coal-derived synthesis gas into liquid fuels, largely due to its relatively simple reactor design, improved thermal efficiency, and ability to process CO-rich synthesis gas. The application of the three-phase slurry reactor system for coal liquefaction processing and chemical industries has recently received considerable attention. To design and efficiently operate a three-phase slurry reactor, the degree of dispersion of the solid (catalyst) in the reactor must be understood and controlled. The solids distribution within the reactor greatly affects its performance. Because it is crucial to understand the influence of various reactions and reactor configurations on the solids concentration profile, measurement of solids concentration must be made under reaction conditions, such as high temperature and pressure, and with the presence of reaction liquid medium.

The ultrasonic technique has advantages over many existing methods because it is a non-invasive and non-destructive measurement in systems which are concentrated, optically opaque, and electrically non-conducting [1]. The utilization of ultrasonic techniques for slurry characterizations has received considerable attention recently [2-9]. A method involving the measurement of ultrasound transmission has been reported recently in a slurry-phase stirred-tank reactor which offers the possibility of using the ultrasonic technique for the measurement of solids concentration in a three-phase slurry reactor [10]. The ultrasonic transmission uses measurements of the velocity and attenuation of the sound wave which travels directly through the slurry sample. When an acoustic wave strikes the boundary between two different media (liquid and solid) and the acoustic impedances of the two media are different, some acoustic energy will be reflected, absorbed, and some will be transmitted. The reflected wave travels back through the incident medium (liquid) at the same velocity. The transmitted wave continues to move through the new medium (solid) at the sound velocity of the new medium. When the velocity of sound in a liquid is significantly different from that in a solid, a time shift (a velocity change) in the sound wave, can be detected when solid particles are present relative to that for the pure liquid. The amplitude of the sound wave is also reduced when a solid particle is present since the wave is partially scattered and absorbed. Therefore, a change in amplitude of the sound wave can also be detected when solid particles are present relative to that for the pure liquid. Okamura et al. [10] used a continuous stirred-tank reactor to correlate the concentration of solids to the relative time shift $((t_a-t_b)/t_o)$. The arbitrary first distinct zero crossing time in liquid and in solid-liquid are defined as t_a and t_b, respectively.

The travel time between the transmitter and receiver in the liquid is defined as t_o. Thus, the concentration of solids in a slurry reactor can be measured by sending an ultrasonic pulse across the slurry and measuring the amplitude and time shift of that portion of the transmitted pulse received at the opposite side of the reactor. Then, comparing the value with those for known concentration, the concentration of solids is determined from the measured signal.

This study examines the possibility of utilizing the ultrasonic technique for slurries concentration measurements in an autoclave reactor under the conditions prevailing in the FT synthesis - temperature of 265°C, glass beads, nitrogen bubbles, and molten FT-200 wax.

Experimental details

The details of the 2.5-liter autoclave reactor in which the ultrasonic investigation was conducted are shown elsewhere [11,12]. The nitrogen flow was controlled electronically to a maximum of 400 ml/min through a mass-flow controller. Glass beads from Cataphote, Inc., (10-37 μm in diameter with density of 2.46 g/cm^3) were used as the solid in the slurry. The concentration of solids (solid weight/total weight) was varied from 1 wt.% to 25 wt.% for each nitrogen flow in the reactor. Molten FT-200 wax (Vestowax), with an average molecular weight of 600, at a temperature of 265 °C, was used as the liquid medium. The density and viscosity of the FT-200 wax at 265 °C are 675 kg/m^3 and 1.9 mPa.s, respectively [13]. Experiments were conducted at 0.1 MPa and 265±0.5 °C in this study. Ultrasonic measurements were taken by using a computer-based TestPro system, manufactured by Infometrics Inc., Silver Spring, Maryland, USA. The details of the ultrasonic unit are reported elsewhere [11,12]. The data were obtained with longitudinal waves at a frequency of 2.5 MHz using lithium niobate transducers (transmitter/receiver). Both the transmitter and receiver were mounted inside a metal adapter which was screwed into a fitting inside the reactor wall. The cooling water was circulated through a cooling collar to the adapter to prevent the transmitter/receiver from being heated.

Results and Discussion

Fig. 1 illustrates the change in the amplitude ratio of the transmitted ultrasonic signals A/A_o in the reactor as a function of nitrogen flow in FT-200 wax at 265°C. A and A_o are the amplitudes of the transmitted signals with and without the presence of nitrogen, respectively. Fig. 1 also suggests that the amplitude ratio is approximately an inverse exponential function of the nitrogen flow. As described in the introduction, the impedances of the two media will determine the transmission of the wave from one medium to another and the amount of reflection of sound at the boundary between the two media. If the impedances of two media are widely separated, e.g., nitrogen and FT-200 wax, then most of the energy is reflected back in the first medium (FT-200 wax) with little transmission into the second medium (nitrogen). It can be assumed that the ultrasonic pulse cannot penetrate through much of the nitrogen/FT-200 wax interface at the current experimental frequency due to the acoustic impedance mismatch of this combination. Therefore, the amount of attenuation of the ultrasound beam by nitrogen bubbles is proportional to the gas volume fraction but also can be dependent on bubble size present in the path of the ultrasound, especially when the ultrasound wave is near the resonance frequency. The attenuation is greatest at frequencies near resonant [1]. For this study, the frequency utilized is not near the bubble resonance frequency. Therefore, the data collected is not affected by the resonance effect. We also measured the bubble sizes under the same experimental conditions through a dual hot-wire anemometer under separate experiments. The majority of the bubble diameters was found to be about 5 mm in the path between the transducer and the receiver within the range of flow studied. The number of bubbles increased as the nitrogen flow rate increased. The decrease of A/A_o as the nitrogen flow increased appears to be related to the bubbles. Chang et al. [14] measured void fractions up to 20% in

bubbly air-water two-phase flow using an ultrasonic transmission technique. Their results showed that the transmitted ultrasonic signal could be approximated by the exponential relationship:

$A/A_o = \exp [-f(d_b)\, \epsilon]$ (1)

where ϵ is the void fraction and $f(d_b)$ is a function dependent on the Sauter mean diameter. This correlation shows that the A/Ao ratio has an exponential relationship with both the void fraction and with a function dependent on the bubble diameter. The effect of air bubble diameter on A/Ao ratio was found to be significant, with A/Ao decreasing with increasing bubble size. Bensler et al. [15] also measured the interfacial area in bubbly flows in air-water systems by means of an ultrasonic technique. Their observations showed that the transmitted ultrasonic signal could also be expressed by an exponential relationship:

$A/A_o = \exp [\Gamma\, x/8\, S(kd_b/2)] = \exp [\Gamma\, x/8\, S(k3\epsilon/\Gamma)]$ (2)

where Γ is the volumetric interfacial area, x is the travel distance in the path, S is the scattering coefficient, k is the wave number of the ultrasonic waves which surround the bubble, ϵ is the gas holdup and d_b is the Sauter mean bubble diameter. Eq. (2) shows that the A/Ao ratio has an exponential relationship with the interfacial area and the scattering cross section, which is a function of both the bubble radius, gas holdup, and the wave number of the ultrasonic wave surrounding the bubble. Our observations of A/Ao in the nitrogen/FT-200 wax system are in qualitative agreement with those reported by Chang et al. [14] and Bensler et al. [15]. The decreasing A/Ao ratio as the nitrogen flow increased in Fig. 1 may be attributed to a combination of the void fraction, bubble size, the number of bubbles, and the scattering cross section. Fig. 1 also shows the effect of the nitrogen flow on the transit time, t. It was approximately 153.2 μs at all nitrogen flows. Apparently the transit time was unaffected by the nitrogen flow under the current experimental conditions. Because what we measured was the signal not transmitted through the nitrogen. Thus, the measured transit time should not be affected by the nitrogen flow. The results indicate that only the amplitude and not the transit time of the ultrasonic signal are affected by the nitrogen flow rate in the reactor under the current experimental conditions. Chang et al. [14] also reported that the amplitude of the transmitted sound pulses depends significantly on the number of bubbles; however, the transit time does not change with the void fraction. Our results obtained from the nitrogen/FT-200 wax system are similar to those of Chang et al. [14] for the air/water system.

Fig.2 further shows the effect of solids concentration on transit time and the amplitude ratio of the transmitted ultrasonic signal A/A_o (A and A_o are the amplitudes of the transmitted signals with and without the presence of solids, respectively) in the autoclave at a constant temperature of 265 °C and with a constant stirring speed and without nitrogen flow. The A/A_o ratio decreased as the concentration of solids increased from 1wt. % to 25 wt.%. In general, the amplitude of the transmitted ultrasonic signals decreased as the solids concentration increased. When an ultrasonic pulse is sent across the slurry reactor, the amplitude of the pulse is reduced when it strikes a solid in the slurry because the pulse is partially scattered and absorbed. The scattering and viscous effects are often the predominant forms of attenuation in heterogeneous materials. The dominating mechanism depends on the range of ka where k is the ultrasound wave number and a the radius of the particle. The scattering regime dominates when $ka >> 1$ while the viscous regime governs for small particle size and lower frequencies ($ka < 1$) [16,17]. For the present study, the ka ranges between 0.18 and 0.68. Thus, the viscous effects dominate over scattering. The latter occurs when some of the ultrasonic wave incident upon a discontinuity in a material, for example, a solid particle, is scattered in directions which are different from that of the incident wave. The unscattered pulse is partially transmitted through the solid at the sound velocity of the solid to the receiver. The amplitude of the transmitted portion of the pulse is measured by the receiver located on the opposite side of the autoclave. The more particles that are present in the path, the less transmitted pulse will be detected. The amplitude ratio of the pulse is inversely proportional to the quantity of solid particles present in the path. Therefore, the measured amplitude of the

sound wave transmitted through a slurry mixture is expected to be a strong function of the concentration of solids. Fig. 2 also presents the effect of the solids concentration on the transit time, t_b. The transit time decreased as the solids concentration increased in the reactor. It was approximately 152.125 μs with 5 wt. % of solids, but decreased to approximately 148 μs as the solids concentration increased to 25 wt.%. When an ultrasound wave strikes the boundary between the FT-200 wax and solids, the acoustic impedances of the two media are different and the ultrasound wave will be partially reflected, absorbed, and transmitted. The reflected wave travels back through the wax at the same velocity (844 m s^{-1} for FT-200 wax at 265 °C). The transmitted wave continues to travel through the solids at the sound velocity of the new medium (5448 m s^{-1} for fused silica at 265 °C estimated from Lynnworth [18]). This explains the decrease in transit time as the concentration of solids increased. Furthermore, the concentration of the solids in the slurry greatly affects both amplitude ratio and transit time, t_b, of an ultrasonic signal. The transit time of the transmitted ultrasonic pulse should depend on the quantity of solid particles present in the path. The higher the concentration of solid particles present in the path, the shorter the transit time that would be observed.

Fig. 3 presents the transit time versus the nitrogen flow up to 300 mL/min at two different solids concentrations, 3 and 25 wt.%. The solids concentrations greatly affect the transit time. It was approximately 152.8 μs at 3 wt.% then decreased further to approximately 148 μs as the solids concentration increased to 25 wt.%. This can be understood by assuming that the presence of solid particles in the path of the sound wave reduces the transit time since the velocity of sound is faster in the solid than in the liquid. The transit time profiles in the range of nitrogen flow studied were rather uniform at both solid concentrations. Thus, one can infer that the variations of nitrogen flow in the reactor did not have significant effects on the observed transit time within the flow conditions studied. The observed, approximately constant transit time at any given constant solids concentration with varying nitrogen flows, illustrates that the detected portion of the sound is not transmitted through the gas.

Fig. 4 further illustrates the fractional change in transit time $\triangle t/t_o$ ($\triangle t = t_a - t_b$) as a function of solids concentration in the absence of nitrogen flow in the stirred reactor. The fractional change in transit time (time ratio) increased as the solids concentration increased. A linear regression analysis was conducted on the collected data. The best fit linear line was also plotted in Fig. 4. The reliability of the regression, R^2 value, is 0.978. For the case of cube root dependence on ω, the R^2 value is 0.781. It is clearly indicated that the fractional change in transit time, $\triangle t/t_o$, has a linear relationship with the concentration of solids. In our previous studies [11,12] under nitrogen/water/glass beads system, a simple model has been proposed for the propagation of sound in very dilute slurries. Our model predicts that the change in time ratio $\triangle t/t_O$ is given by the relation

$$\triangle t/t_O = \alpha\, \omega^{1/3}(1- v_l/v_S) \qquad (3)$$

Here α is a constant for particles of a given composition and v_l and v_S are the speed of sound in the liquid and solid, respectively. ω is the solid concentration fraction. However, this expression does not give the correct dependence on solids concentration nor its magnitude.

Urick [19] has proposed a phenomenological approach to correlate the solids concentration and velocity of sound through the medium. The coupled-phase model of suspensions approaches have also been investigated by Harker and Temple [20]. These approaches can be applied to further theoretical study.

The results from our study are in qualitative agreement with those previously reported by Okamura et al. [10]. Our results with molten wax are similar to the previous results from the nitrogen/water/glass beads system [11,12] although our previous results give larger values of time ratio at a given solids concentration fraction than our current nitrogen/FT-200 wax/glass beads data. A possible explanation of the discrepancy could be that the geometry of our previous apparatus, nitrogen/water/glass bead system at ambient conditions differs considerably from that employed in the current study (autoclave reactor, nitrogen/FT-200 wax/glass

beads system, and 265 °C). In general, both the amplitude and the fractional change of transit time (or time ratio) were affected by the variation of solids concentrations. It appears that the time ratio depends mainly on the solids concentration. The variation of nitrogen flow has little effect on the observed fractional change of transit time (or time ratio) within the flow conditions studied. Based on these results, it can be concluded that the ultrasonic technique has potential applications for solids concentration measurements in three-phase slurry reactors at high temperatures.

Conclusion

The results presented in this study led to the conclusion that both the amplitude and the transit time of an ultrasonic signal are influenced by the variation of solids concentration in molten FT-200 wax. The variation of nitrogen flow has little influence on the observed transit time within the conditions studied. The ultrasonic technique has potential applications for solids concentration measurements in three-phase slurry reactors at elevated operating temperatures.

References

1. D. J. McClements, *Adv. Colloid Int. Sci*., 37 (1991) 33.
2. L. R. Abts and P. H. Dahi, *US Patent* 4,580,444, 1986.
3. K. G. Foote, *US Patent* 4,527,420, 1985.
4. C. E. Behrman and J. W. Larson, *MBAA Tech. Qu*., 24 (1987) 72.
5. W. Hilgert and H. Hofmann, *Ger. Chem. Eng*., 9 (1986) 180.
6. J. C. Bonnet and L. L. Tavlarides, *Ind. Eng. Chem. Res.,* 26 (1987) 811.
7. C. Tsouris, L.L. Tavlarides and J. C. Bonnet, *Chem. Eng. Sci*., 45 (1990) 3055.
8. C. Tsouris, M. A. Norato and L. L. Tavlarides, *Ind. Eng. Chem. Res*., 34 (1995) 3154.
9. A. Warsito, A. Maezawa, S. Uchida and S. Okamura, *Can. J. of Chem. Eng*., 73 (1995) 734.
10. S. Okamura, S. Uchida, T. Katsumata, and K. Iida, *Chem. Eng. Sci*., 44 (1989) 196.
11. Y. Soong, A. G. Blackwell, R. R. Schehl, M. F. Zarochak and J. A., Rayne., *Chem. Eng. Comm*., 138 (1995) 213.
12. Y. Soong, I. K. Gamwo, A. G. Blackwell, R. R. Schehl and M. F. Zarochak., *Chem. Eng.* J., 60 (1995) 161.
13. D. B. Bukur, J. G. Daly, S. A. Patal, M. L. Raphael and G. B Tatterson, DOE Final Report, DE-AC22-84PC70027, (1988), p. 219.
14. J. S. Chang, Y. Ichikawa, G. A. Irons, E. C. Morala, and P. T. Wan, in J. M. Delhayeand G.Cognet(eds), *Measuring Techniques in Gas Liquid Two-Phase Flows*, Springer, 1984, p. 319.
15. H. P. Bensler, J. M. Delhaye and C. Favreau, *Proc. ANS Nat. Heat Transfer Conf*., 1987, p. 240.
16. J. S. Derksen and H. K. Kytömaa, *ASME*, 189 (1994) 75.
17. H. K. Kytömaa, *Power Technol*, 82 (1995) 115.
18. L. C. Lynnworth, *Ultrasonic Measurements for Process Control*, *Academic Press, San Diego, CA, (1989).*
19. J. R. Urick, *J. Acoust. Soc. Am*. 18 (1947) 983.
20. A. H. Harker, and J. A. G. Temple., *J. Phys. D: Appl. Phys*. 21 (1988) 1576.

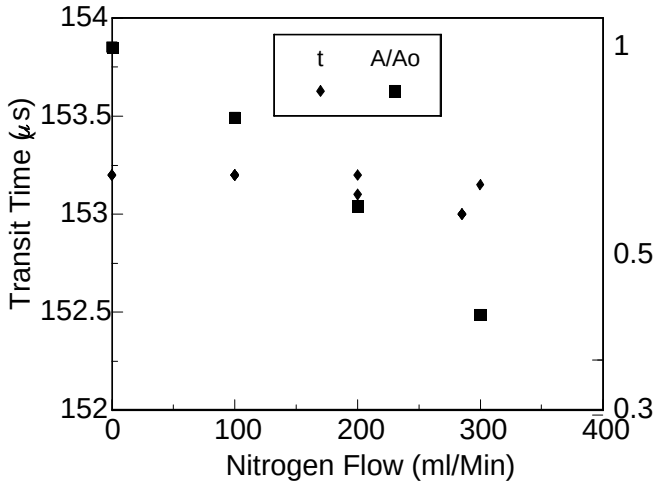

Fig. 1. Amplitude ratio and transit time as a function of nitrogen flow in FT-200 wax at 265°C.

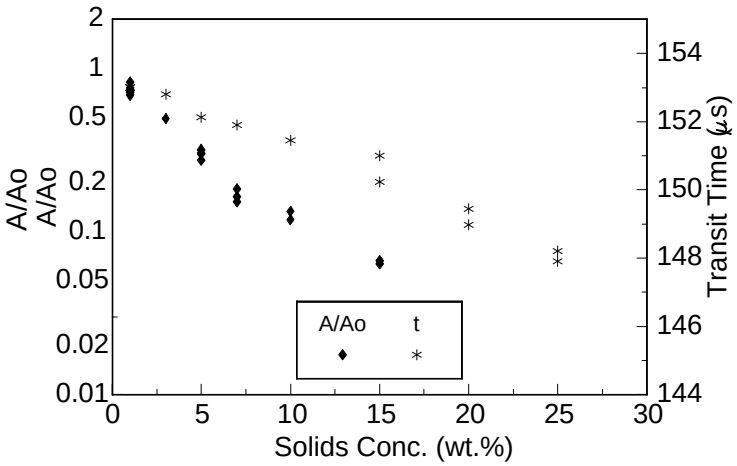

Fig. 2. Amplitude ratio and transit time as a function of solids concentration (wt. %) in FT-200 wax.

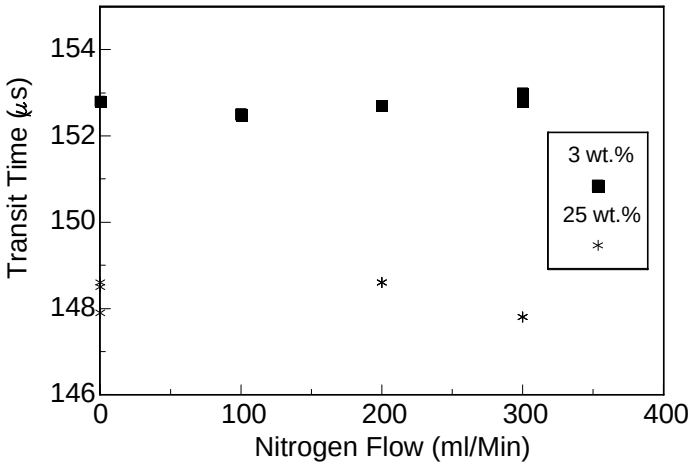

Fig. 3. Transit time as a function of nitrogen flow in FT-200 wax at two different solids concentraions.

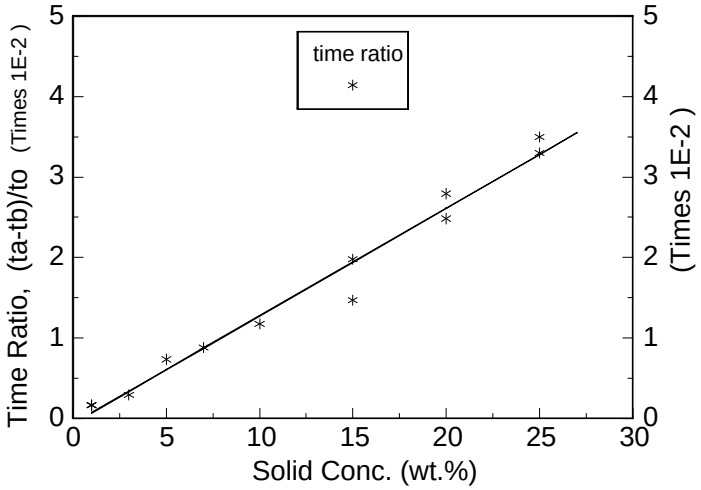

Fig. 4 Time ratio as a function of solids concentration (wt.%) in FT-200 wax