Monitoring polymerization

LiquiSonic® Application Report

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Directory

LiquiSonic® Method

LiquiSonic® is a highly sophisticated inline/in-situ liquid analyzer well-suited to biotechnological, pharmaceutical, supersaturation, concentration and crystallization processes. Using sonic velocity and temperature measurement technology combined with a unique sensor design, the system allows control and monitoring of concentrations and general process trends at different points.

LiquiSonic® supplies the operator with real-time knowledge needed to optimise the process. A **LiquiSonic®** system consists of one or more intelligent sensors and a controller connected to each other by a digital line.

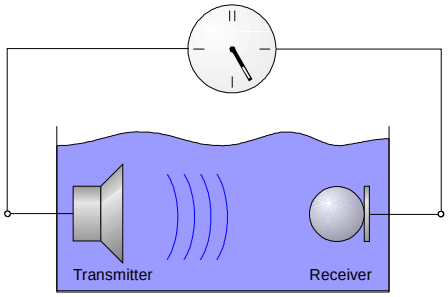
In addition, modern manufacturing technologies guarantee precise measuring results and convenient device operation. This includes the simultaneous presentation of mass-concentration or crystal content, product temperature, and product or recipe identifiers.

The data memory and event tracking capabilities (according to FDA 21 CFR Part 11) in conjunction with user-defined passwords ensure a maximum degree of process and application safety and security.

A multi-channel, real-time chart and the non-volatile configuration and process data RAM card allow easy system adaptation for lab, pilot, or production scale applications.

LiquiSonic® sensors are available in different designs and process fittings to suit tubes or vessels. For installations in hazardous areas, an explosion proof sensor is available. All sensors can be equipped with an electro-polished finish, and all sensors may have an ultra-sanitary design without gaskets to handle the toughest process environments and typical CIP / SIP procedures.

All systems include inline validation capability, which guarantees precise, traceable, and reproducible results under every circumstance.



Introduction

In connection with the need to closely monitor and control processes, the capability to determine conversion in chemical reactions in general and in particular in polymerization reactions is of outstanding significance.

Just like concentration measurements, conversion measurements are becoming more and more important in all branches of industry on account of their impact on the efficiency of processes, their potential for material and energy savings, quality improvements as well as for environmental reasons.

For measuring concentrations and conversion, a number of process measuring methods have been developed, including methods based on density measurement, refraction index measurement, conductance measurement, the measurement of colour, turbidity and viscosity, all of these methods being characterized by specific physical and technological limitations.

It has been known for quite some time that concentrations can be determined by measuring ultrasonic velocity, and this method has become the standard measuring technique in recent years.

Ultrasonic sensors with greatly improved technical parameters have made the determination of concentrations and conversion in polymerization reactions a highly promising field of application of ultrasonic measuring technology.

This paper provides a description of the determination of concentrations and conversion in liquid systems, specifically in polymerization reactions.

Physical foundations

The propagation velocity *v* of ultrasonic waves in liquids is dependent on their density and adiabatic compressibility in accordance with the following relationship:

$$v^2 = \frac{1}{\rho^* \beta_{ad}}$$

v	=	sonic velocity
ρ	=	density
β_{ad}	=	adiabatic compressibility

The fact that the compressibility is the determining variable for the sonic velocity causes that, as the sonic velocity increases, density and compressibility may show a differing behavior. This, in turn, causes that even if there are only minor differences in density or none at all, large differences in the sonic velocity may occur. It very rarely happens that the reverse case takes place. This phenomenon has consequences for measuring applications, since it offers the possibility to use ultrasound for measuring concentrations in cases in which density measurements fail to yield the desired results.

As both density and compressibility are temperature dependent, material specific constants, the sound propagates in each material at a characteristic velocity, which depends on the temperature. With gases, the sonic velocity is less than 700 m/s, for liquids, it is in the range from 700 to 2,500 m/s, and for solids, it may reach up to 7,000 m/s. The sonic velocity is determined by the structure of the material concerned, that is, by groups of atoms and molecules, isomerisms or chain lengths. This correlation, thus, allows to characterize materials with the help of ultrasound.

The table below shows the sonic velocity *v* of a few selected monomers and polymers at 20°C.

Monomer	v [m/s]	Polymer	v [m/s]
Styrene	1.354	Polystyrene solid	2.330
Vinyl chloride	897	Polyvinyl chloride solid	2.260
Vinyl acetate	1.150	Polyvinyl acetate dispersion 50 wt %	1.940
Butyl acrylate	1.233	Polybutyl acrylate dispersion 50 wt %	1.375
Butadiene	961	Polybutadiene solution 20 wt %	1.373
Water	1.482		

As concerns monomer and polymer systems, it generally applies that the differences existing in the sonic speed between monomers and polymers are primarily determined by the chain length and the extent of their branching and cross-linking.

In multi-component systems, the sonic velocity depends on

- the sonic velocity of the individual components,
- the state - temperature and pressure,
- the composition,
- the interactions between the individual materials.

Consequently, it is principally possible to determine the composition of multi-component systems, provided that all influence factors are known.

In liquid multi-component systems, the overall sonic velocity is dependent on the sonic velocity of a liquid carrier and the contributions made by the individual components A ..... X:

$$v = v_A + \Delta v_B + \Delta v_C + \Delta v_D + \Delta v_E + ... + \Delta v_X$$

In polymer systems based on emulsion polymerization:

A = water
B = monomer
C = polymer
D = initiator
E = stabilizer

The contribution of the individual components, in turn, is dependent on the specific contribution, expressed as sonic velocity-concentration coefficient, and on the concentration:

$$\Delta v = k * \frac{\Delta v}{\Delta k}$$

Thus, to be able to determine the concentration and conversion by measuring ultrasonic velocity, you have to know the temperature dependence of the sonic velocity-concentration coefficients of all components.

Typical polymer systems

The fundamental correlations described above have been verified in the past in a number of polymerization reactions:

- solvent polymerization of butadiene
- emulsion polymerization of vinyl acetate
- emulsion polymerization of butadiene and styrene
- emulsion polymerization of vinyl chloride
- emulsion polymerization of acrylates
- suspension polymerization of styrene
- suspension polymerization of vinyl chloride
- polycondensation of urea and formaldehyde
- polycondensation of phenol and formaldehyde

Typically, the sonic velocity of all components involved is determined as a function of temperature. From the time course of the sonic velocity, you can then derive the course of reaction and calculate the materials conversion.

Emulsion polymerization of butadiene and styrene

The individual components and lattices were examined for a butadiene-styrene emulsion polymerization reaction system.

It can be seen that the sonic velocity of the monomers clearly differs from that of the polymers (Fig. 1). The course of variation of the sonic velocity during polymerization is shown in Fig. 2.

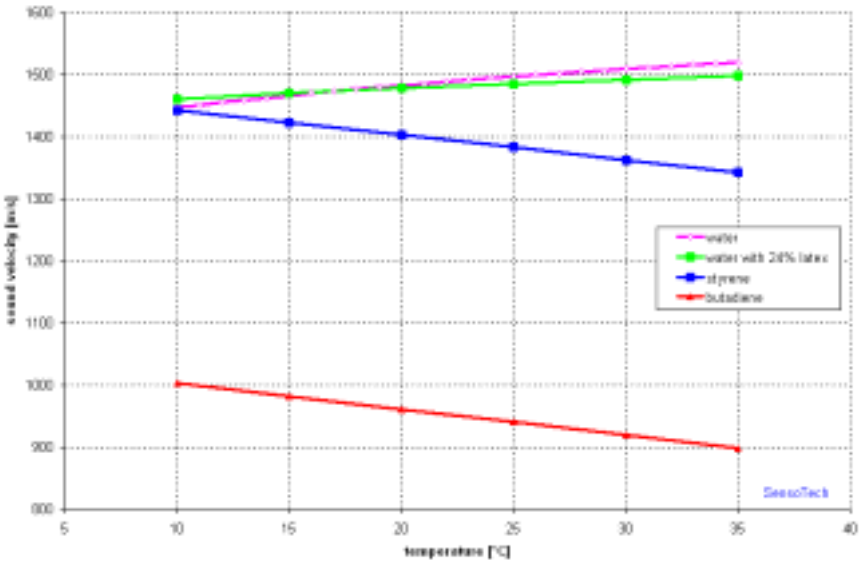


Fig. 1: Sonic velocity of components of butadiene-styrene polymerization.

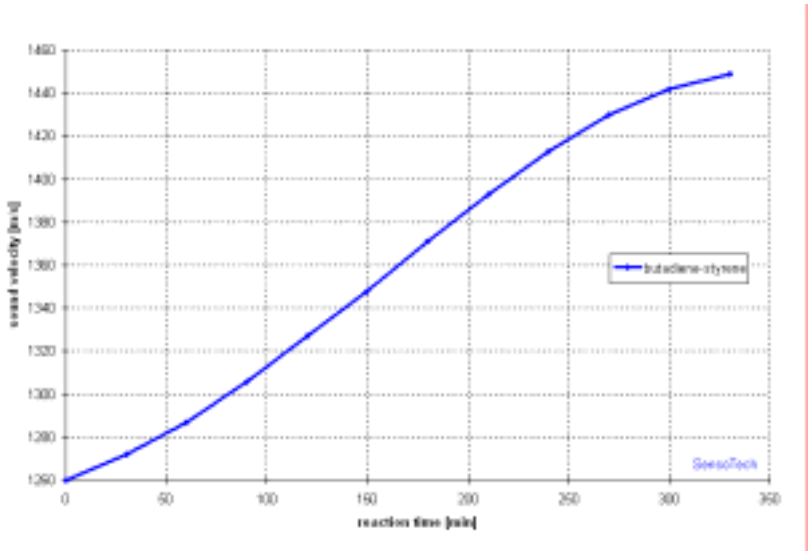


Fig. 2: Variation of sonic velocity during polymerization of butadiene and styrene.

In the emulsion polymerization of butadiene and styrene, conversion can be determined to within 0.1 conversion %.

Solvent polymerization of butadiene in toluene

As an example of solvent polymerization, the polymerization of butadiene to 1,4-cis polybutadiene is shown. Here, the conditions are not so complex, because we have to do only with a liquid phase. The reaction takes place at approx. 70 °C, the butadiene content in the solvent, toluene, being 13 wt %.

The accuracy of the conversion measurement is dependent in this case on the difference between the velocity of sound in the solvent with the monomer and that in the solvent with the polymer. It is 0.2 conversion % (Fig. 3).

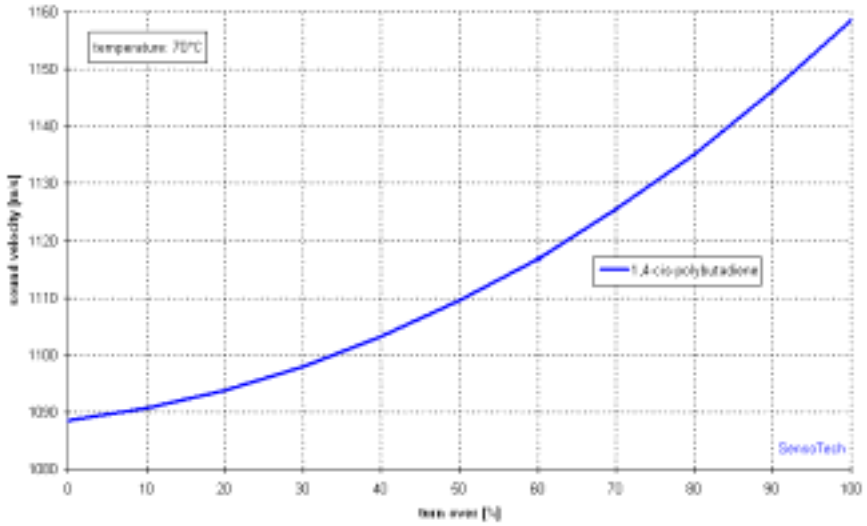


Fig. 3: Materials conversion in butadiene to 1,4-cis-polybutadiene polymerization

Suspension polymerization

As examples of suspension polymerization, the polymerization of styrene and vinyl chloride is shown.

Here, the reaction conditions are much more complex, because there are liquid and solid phases, and the morphology of particles strongly varies during the process.

Fig. 4 shows the velocity of sound during the reaction process in the suspension polymerization of vinyl chloride and styrene.

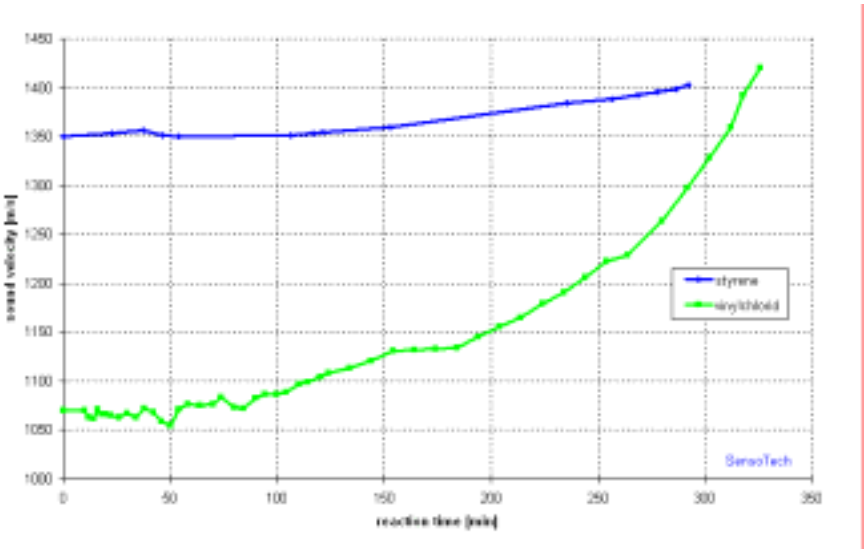


Fig. 4: Sonic velocity during polymerization of vinyl chloride and styrene

The difference between the sonic velocity existing at the beginning of the reaction and that at the end of the reaction is much higher in the polymerization of vinyl chloride so that conversion can also be determined with a better accuracy.

Ultrasonic measuring equipment

Ultrasonic measuring systems are nowadays widely used in almost all branches of industry where concentrations need to be measured and variables derived therefrom such as conversion and reaction rates have to be determined.

These measuring systems offer the following advantages:

- high accuracy
- outstanding robustness
- contactless measurement
- suited for use in all liquid systems (solutions, emulsions, dispersions, suspensions) including liquid systems with a very high solids content
- no harmful side effects
- long-time stability
- range of sensors for all operating conditions available

Ultrasonic measuring devices can be used in the following phases:

- determination of concentration of monomers
- monitoring of polymerization, materials conversion
- determination of concentration of polymer

In polymerization monitoring applications, ultrasonic measuring systems have distinct advantages in comparison with other measuring techniques. Ultrasonic sensors may be used at high pressures and temperatures. Moreover, probes are available which do not cause reductions in the cross-section of pipelines. Probe manufacturers offer probes made from a range of different materials and exhibiting various surface finishes.

The ultrasonic probes may be of the tubular or immersion type. (Fig. 5). A tubular probe is screwed in into a pipeline directly between two flanges.

Several probes may be connected to an evaluating unit (controller) so that cost-efficient measurements can also be performed in multi-stage reactors.

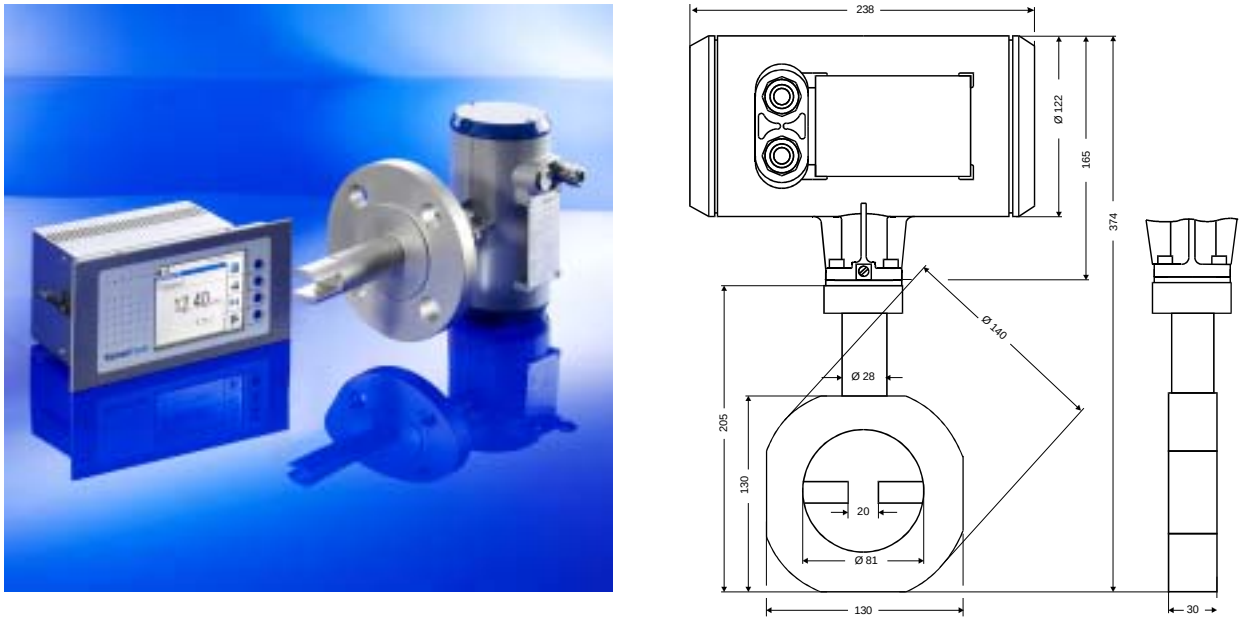


Fig. 5: **LiquiSonic** Ultrasonic measuring device with immersion and tubular probe

A PC software like **SonicWork** allows the monitoring of the polymerization process.

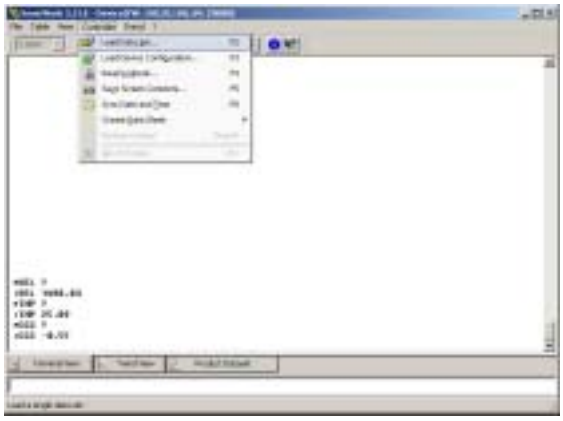


Fig. 6: SonicWork,

Chart

Summary

The capability to precisely determine materials conversion during polymerization processes offers the following benefits:

- improved economy of the process with respect to material and energy,
- improved, more uniform quality,
- allows optimization of downstream process stages.

It is becoming more and more clear that ultrasonic methods will become the standard measuring methods for determining concentrations, densities and materials conversion.

Herstellung

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SensoTech

For almost 20 years **SensoTech** has been primarily focused on the development, production, marketing. and support of high-performance in-line analyzers for concentration, density, or the monitoring of complex chemical reactions in liquid systems. During this time, **SensoTech** has an overall installation base of over 2000 devices worldwide. The unique products offer optimized and cost saving solutions for virtually every kind of application and process.

Providing solid solutions to complex problems has been both the challenge and the cornerstone of the **SensoTech** business. With the global installations and an extensive range of innovative products, **SensoTech** offers affordable, efficient solutions that meet our clients' exacting needs in food and beverage production and in chemical, pharmaceutical, biotechnical, semiconductor, iron and steel industries.

With **SensoTech**, cost-effective equality control, reduced developmental expenditures, optimized benchmark processes, and elevated standards are attainable.

What makes **SensoTech** valuable:

- Established experience
- Application Knowledge
- Superior Technology
- Proven performance
- Extremely Tough, Reliable and Low Maintenance equipment
- Unbeatable warranties, service, and support

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