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A Continuous Process for Casein Production Using High-pressure Carbon Dioxide*

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ABSTRACT

A continuous process for protein production that uses high-pressure carbon dioxide (CO₂) instead of organic acids as precipitant has been used to isolate casein from milk. Central to the process is a pressure reduction stage that follows a reaction/precipitation stage, in which protein produced in the reactor may be removed without depressurizing the reactor and subjecting the products to excessive shear. Two reactor/precipitators were designed and tested. One was a spray reactor in which milk and CO₂ were contacted by spraying milk into CO₂. The other was a tubular reactor fed a mixture of liquid CO₂ and milk. Both reactors gave casein products of good quality, but casein yield from the tubular reactor was greater than that from the spray reactor. The methods presented here may be extended to other processes that currently use organic acids for precipitation or supercritical extraction systems at pressures less than 15000 kPa for continuous transport of solid-liquid mixtures from high-pressure units to atmospheric pressure.

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INTRODUCTION

Food proteins such as casein are usually recovered using isoelectric precipitation. Casein is isolated through the action of lactic acid-producing bacteria or by a mineral acid such as HCl or H₂SO₄ at its isoelectric point of pH 4.6. In casein manufacture, the precipitation step is followed by a holding or acidulation stage for agglomeration of the curd and stages for casein and whey separation, casein

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washing, drying, and milling (Southward & Walker, 1980). The whey may be treated using ultrafiltration or diafiltration to produce whey protein concentrates (Morr, 1989).

As shown in a series of batch studies (Jordan *et al.*, 1987; Tomasula *et al.*, 1995), casein may also be precipitated by H_2CO_3 , formed by reaction between CO_2 and the endogenous water in milk. Optimal product was produced in the 4000–6000 kPa pressure range and in the 38–49°C temperature range. Above 60°C, casein had a dried out appearance with no discernible particles.

There are advantages to using CO_2 instead of lactic or mineral acids for casein precipitation. Because of the relatively high residual pH of 6.0, the whey would require less pretreatment for further processing and present less of a disposal problem than conventionally produced whey with a pH of 4.6.

Batch processes that utilize high-pressure CO_2 , supercritical CO_2 or any other suitable gas are effective for recovery of small amounts of high-valued products. Large-scale batch production requires significant downtime for depressurizing, cleaning and refilling. Economic production of food proteins requires a continuous process consisting of a reactor/precipitator and a method for continuous pressure reduction.

Reactor/precipitator design requires knowledge of the coagulation time of the protein and consideration of the manner in which the reactants are contacted for optimal quality and yield. Coagulation time for casein precipitated by CO_2 has not been determined accurately. Jordan *et al.* (1987) showed in a 120 ml reactor that the same amount of CO_2 -precipitated casein was obtained in a run carried out for 1 min as that carried out for 5 min. Tomasula *et al.* (1995), working with a 1 liter batch reactor, showed that coagulation time was at most 5 min for formation of CO_2 -precipitated casein. Difficulties in manipulation of the pressurized reactors prevented establishing exact coagulation times.

Muller and Hayes (1962) showed that coagulation became apparent about 0.1 s after mixing acid with skim milk at 43–46°C. Jablonka *et al.* (1988) showed in light scattering experiments of batch and continuous reactors at varied temperatures and pH that coagulation time for casein precipitated by mineral acid is less than 1 s. Acid/milk mixing was identified as the rate-controlling step for formation of precipitate and was critical to curd development.

Coagulation rate control is also an important consideration in reactor/precipitator design because it affects curd quality. Muller and Hayes (1962) attributed a sticky curd or one that disintegrates on further processing to precipitation at $\text{pH} \geq 4.4$ at higher temperatures. Methods for regulation of coagulation rate included lowering mixing temperature and the use of pumps to ensure a constant flow of milk and acid. Milk–acid mixture was gradually heated to the coagulation temperature and then held for curd agglomeration prior to casein–whey separation. Jablonka and Munro (1986) also found that particle size, solids content, cohesiveness and firmness increased with increasing precipitation pH and temperature and correlated with higher curd Ca content.

For continuous recovery of CO_2 -precipitated casein, it is necessary to maintain the reactor at system pressure while removing the precipitate and whey. Another requirement for continuous recovery is maintaining the integrity of the casein curd. Particle size distribution (PSD) is used as a measure of the quality of freshly precipitated casein (Jablonka & Munro, 1986). While quantitative standards do not exist for PSD of wet casein, it is generally accepted that freshly precipitated casein

be comprised of distinct curds. Larger curds are desirable because they are easily transported and handled, with minimal losses, in the subsequent washing and drying steps encountered in casein manufacture. Small particles tend to be soft. Fused particles, an indication of heat damage, are unacceptable because they tend to be tough and rubbery, making them difficult to handle in subsequent operations.

Batch experiments have shown that casein particles may be as large as 6 mm (Tomasula *et al.*, 1995). Proposed methods for continuous recovery of solids from high-pressure or supercritical systems in the literature are scarce. Rice (1988) proposed a method for continuous recovery of soybean flakes extracted with CO₂ from a high-pressure or supercritical system in which it is claimed that the extracted flakes are compacted and discharged through a cone valve at the exit of a screw press while maintaining system pressure. The integrity of the particles is not maintained as the compacted flakes are slowly forced out through the tapered sides of the valve opening.

This study was conducted to develop a reactor/precipitator for continuous production of casein using high-pressure CO₂ and a method for continuous removal of the precipitate from the pressurized reactor. A tubular reactor/precipitator and a spray reactor/precipitator were fabricated to contrast types of mixing patterns, coagulation rate control, and residence time on casein quality.

EXPERIMENTAL SECTION

Pasteurized, homogenized skimmed milk from a commercial dairy was used in all runs. The average analysis of the milk was: solids content, 9.0%; ash content, 0.7%; Ca content, 1.3% (dry basis); Na content, 0.5% (dry basis); lactose, 4.6%; and, protein content, 3.19%. The average pH of fresh milk was 6.70. CO₂ (Airco, Murray Hill, NJ) was fed from cylinders equipped with dip tubes.

Equipment

The pilot-plant process scheme for continuous production of casein and whey is shown in Fig. 1. Milk and CO₂ were fed to the reaction/precipitation stage which consisted of either of the high-pressure reactors discussed below. Pressure was reduced in the second stage. After a holding period of about 10 min, casein and whey were separated. In the next stages, casein was washed, dewatered, dried and milled. The whey was filtered to remove any fines and then dried.

Two types of reactors were designed and tested in the reaction/precipitation stage; a spray column and a double-pipe tubular reactor. The double-pipe tubular reactor is shown in Fig. 2 and consists of a section for contacting milk and CO₂, a double-pipe section for heating the cold milk-CO₂ mixture to precipitation temperature and a non-jacketed section that leads to the reactor outlet. It was constructed on the same scale as the batch reactor discussed previously (Tomasula *et al.*, 1995) and has a volume of 1 liter. The reactants were mixed at low temperatures to enhance the solubility of CO₂ (Dodds *et al.*, 1956). Milk at 4°C was pumped from the feed tank by the Rannie pump to a 4.5 m section of high-pressure tubing. Liquid CO₂ at 6°C was pumped into the flowing milk stream at five points along the tube using a Milton Roy Milroyal C (Milton Royal Flow Control Division, Ivyland, PA) packed plunger liquid end pump with a plunger diameter of 2.9 cm and a maximum dis-

charge pressure of 11000 kPa. The pump was equipped with a cooling jacket. Pressures less than 5520 kPa were not investigated because the CO₂ feed pump requires an inlet feed of at least 4800 kPa. A static mixer (Admixer, Inc., Londonderry, NH) at the end of this section facilitates mixing. The jacketed portion is a 17.1 m double-pipe tubular reactor consisting of an inner tube of nominal 1.3 cm high-pressure tubing (1.0 cm i.d.) and an outer tube of 2.54 cm copper tubing. The temperature of the reactor is controlled by hot water flowing countercurrently to the milk-CO₂ stream. (Although not shown, thermocouples were placed along the bends of the reactor on the Moyno side.) This section is followed by another straight length of tubing. The working pressure of this reactor is 10000 kPa.

The flow rates of milk and CO₂ were approximately 55 kg/h and 2 kg/h, respectively, for the laminar flow runs ($N_{Re} = 1700$). Residence time was approximately 1 min. Flow rates of milk and CO₂ for the turbulent flow runs were 120 kg/h and 5 kg/h ($N_{Re} = 4000$), respectively, with a residence time of 0.5 min. The amount of CO₂ required for precipitation of casein from milk corresponds roughly to its solubility in water at system temperature and pressure. Solubility data for CO₂ in water as a function of pressure may be found in Dodds *et al.* (1956). At 38°C and 5520 kPa, CO₂ solubility in water is approximately 4.3 g CO₂/100 g H₂O; at

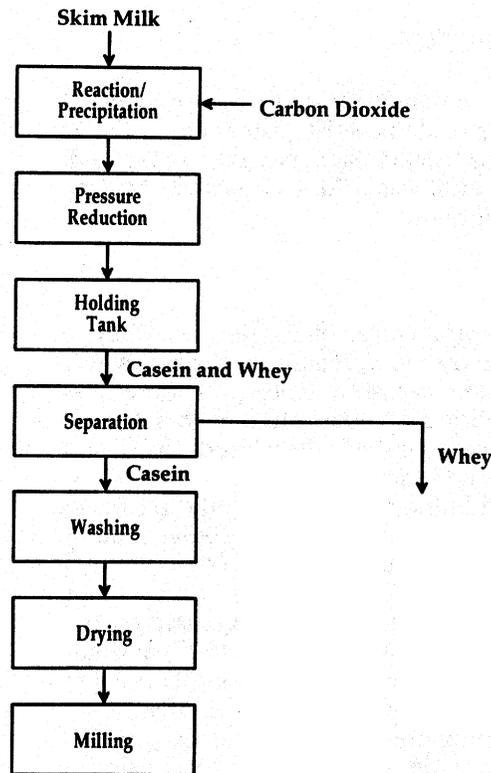


Fig. 1. Pilot plant process scheme for continuous precipitation of casein and whey.

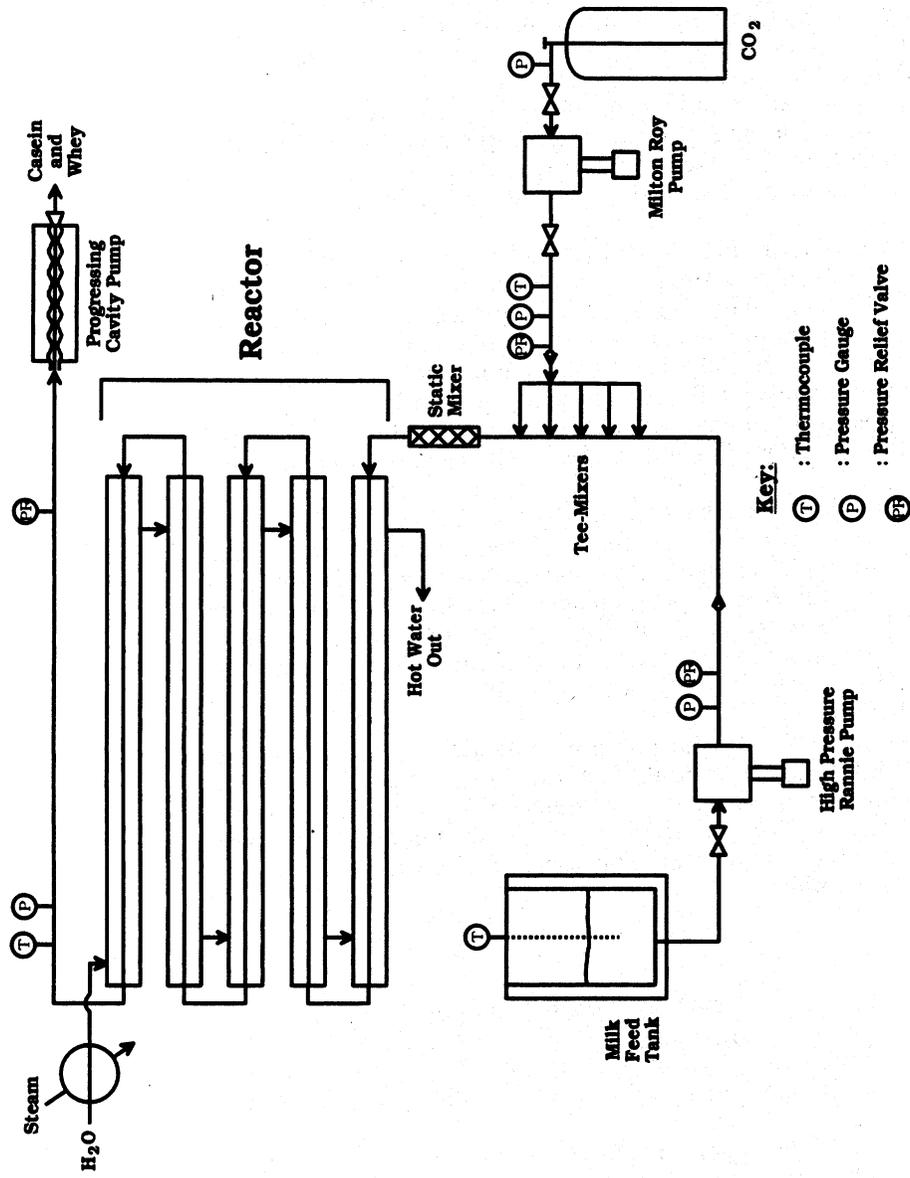


Fig. 2. Double-pipe reactor/precipitator.

6900 kPa, CO₂ solubility is 4.6 g CO₂/100 g H₂O; and at 7580 kPa, CO₂ solubility is 5.0 g CO₂/100 g H₂O.

The Moyno Progressing Cavity Pump (Robbins and Myers, Inc., Springfield, OH), fed through the discharge end and operated in reverse, was used to pump the casein and whey from the pressurized reactors down to atmospheric pressure. The pump is equipped with a food-grade nitrile stator and a 316 ss rotor. The pump has a capacity of 9 liter/min and a working pressure of 15 000 kPa.

In a typical run, the system was operated by turning on the Rannie and then the speed of the Moyno was adjusted to give desired system pressure. The Milton Roy was then turned on to feed CO₂ to the reactor. pH of the whey and casein curd was also measured. Runs were carried out at 32, 38, 43, and 49°C and at pressure of 5520, 6900, and 7580 kPa.

The spray-fed reactor is shown in Fig. 3. It was built from 0.9 m of nominal 12.7 cm Schedule 120 Type 316 stainless steel seamless pipe (i.d. 11.7 cm). Reactor volume was approximately 10 liters. The top threaded nut accommodated a milk feed line, a CO₂ feed line, a pressure gauge, and a thermocouple. The bottom threaded nut accommodated a casein and whey product line and a thermocouple. Milk was sprayed into the reactor using a 0.3 cm spray nozzle tip (Spraying Systems Co., Wheaton, IL). Removable trays to provide additional surface area for milk and CO₂ contact were tried but were found difficult to clean. The reactor has a working pressure of 21 000 kPa.

To prepare the reactor for operation, the walls of the reactor were preheated to the desired temperature. The reactor and CO₂ feed line were wrapped in heating tape. Valve A was closed and milk supplied from the heated feed tank was then pumped to the spray head using the Rannie pump. The reactor was filled to a height of 0.3 m. CO₂ was allowed to flow freely to fill the cylinder to desired pressure. Valve A was then opened and then speed of the Moyno pump was adjusted to maintain desired pressure. Runs were carried out at 32, 38, 43, and 49°C and at pressures of 4130 and 5520 kPa.

Casein and whey removed from the Moyno pump were held for 10 min and then separated using a Sparkler filter (Sparkler Manufacturing, Inc., Mundelein, IL) to simulate the washing and dewatering stages of a commercial operation. Whey was drawn off and casein was collected on the trays of the filter. Water at 40°C was pumped through the filter to wash the casein. The casein was dried in a vacuum drier and then milled in a Wiley mill.

Analysis

Casein and whey samples were taken in triplicate at each unit operation. Solids, ash, Ca, and lactose were determined as described previously (Tomasula *et al.*, 1995). Total protein content was estimated using the Coomassie dye binding method (Bradford, 1976) with sodium caseinate in urea buffer as the standard (Douglas *et al.*, 1982).

The HPLC method described previously (Tomasula *et al.*, 1995) was used to determine the relative weight percentages (wt/wt) of the major milk proteins for some of the casein and whey samples.

Casein and whey were collected from either reactor and particle-size distribution was determined using a wet-sieving method (Jablonka & Munro, 1985). The smallest particle size that could be measured was 43 μm.

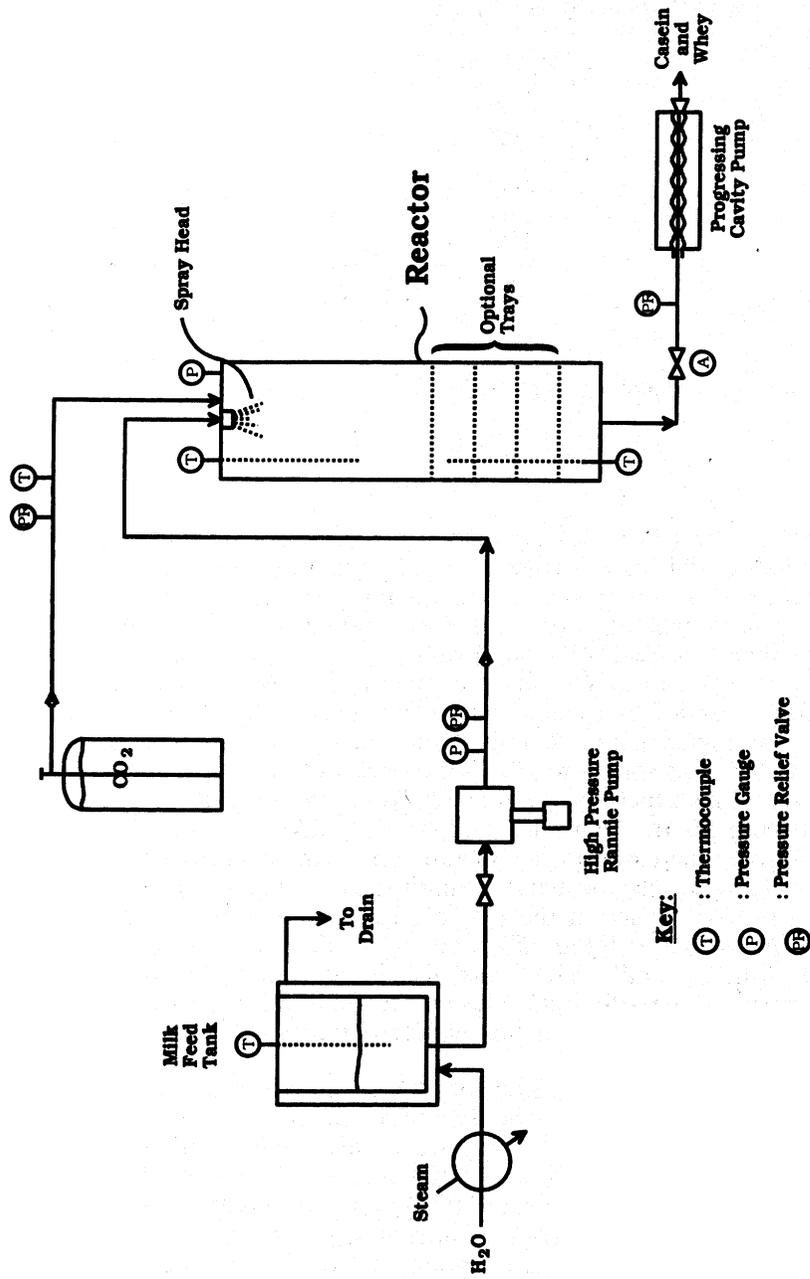


Fig. 3. Spray fed reactor/precipitator.

TABLE 1
Amount of Casein Recovered Because of Changes in Mixing Configuration of Tubular
Reactor: $T = 38^{\circ}\text{C}$, $P = 5520 \text{ kPa}$, $N_{\text{Remilk}} = 4000$

<i>Mixer configuration</i>	$N_{\text{reCO}_2}/\text{Tee}$	<i>Yield</i>
Single-tee	14000	nil
Two tees	7000	nil
Five tees	2800	0.5
Static mixer+one tee	14000	1.5
Static mixer+five tees	2800	2.8
Static mixer+five tees	2800	2.8 ^a

^a $N_{\text{Remilk}} = 1700$.

RESULTS AND DISCUSSION

Mixing of reactants

Continuous tubular reactor

Best contact between cold milk and CO_2 occurred when a static mixer was placed downstream of a series of 90° tee mixers as shown in Fig. 2. Yield of casein leaving the reactor was used to define good mixing because it was not possible to carry out tracer studies of the pressurized reactor. Complete precipitation was assumed if yield of casein was greater than or equal to 2.8% of the weight of milk (Tomasula *et al.*, 1995). Table 1 presents yield for some mixer configurations. N_{Re} of CO_2 in each tee is also given. Little casein was obtained using up to two 90° tee mixers where an excess of CO_2 was mixed with the milk feed. Yield was improved by increasing the number of tees and is shown for five tees, decreasing the amount of CO_2 fed from each tee. Even though the flow rate of CO_2 was in the fully developed turbulent regime ($N_{\text{Re}} \geq 10000$) for the single tee and that of milk was in the low turbulent regime, $N_{\text{Re}} = 4000$, an increased milk flow rate, above the capacity of the pump used in these experiments, would most likely eliminate the need for a static mixer and promote mixing in the first leg of the reactor. The five tees allowed for decreased amounts of CO_2 in contact with the milk feed and greater absorption and mixing of the liquid CO_2 with the milk. Yield was also greater than 2.8 under laminar flow conditions. Attrition of protein particles by the static mixer was not a concern because precipitation does not occur at the low temperatures of the mixing section of the reactor (Tomasula *et al.*, 1995).

Because coagulation time is not presently known for CO_2 precipitated casein, the reactor was sized so that a coagulation or residence time of 5 min could be achieved, even at low flow rates of milk. Preliminary runs showed that residence times of 1 min (laminar flow) or 0.5 min (turbulent flow) were adequate for achieving high casein yield. This was expected because of the relatively short coagulation times given for milk precipitated by mineral acids (Muller and Hayes, 1962; Jablonka *et al.*, 1988). Additional time is not needed for absorption of CO_2 in milk because absorption of CO_2 in water and subsequent formation of H_2CO_3 is rapid (Danckwerts, 1970) and assuming absorption rates are nearly the same for CO_2 in milk (91% H_2O), the rate of absorption in milk may also be assumed to be rapid.

Because control of coagulation rate impacts product quality (Muller and Hayes, 1962; Jablonka and Munro, 1986) reactor contents were brought from 4°C to 30°C at the rate of 4.2°C/m in the first two passes and then to 38°C along the remaining length of the reactor. Precipitate formation most likely occurs when temperature reaches 25°C, in the second pass (Tomasula, 1995).

Spray-column reactor

Mixing between milk and CO₂ was accomplished by spraying droplets of milk into a column of gaseous CO₂. Holdup volume was 1 liter. The holdup of liquid in the reactor assures additional contact time between the reactants; however, this volume is stagnant and further mixing between the reactants does not occur. In addition, there is no means of controlling coagulation rate as there is in the tubular reactor. This method of contacting the reactants was insufficient for reaction because values of yield averaged <2.8%. Mixing the reactants at the higher temperatures, instead of at 4°C, introduced only about 3.1 g CO₂/100 g H₂O unlike 7 g CO₂/100 g H₂O introduced at the feed mixing section for the tubular reactor. Improvements in yield were not obtained by varying CO₂ pressure or temperature. Increasing holdup or residence time by reducing the flow of milk to the reactor and the removal of products did not improve yield, nor did the introduction of trays to the reactor to increase contact time between the milk droplets and CO₂.

Product removal

Initial experiments were conducted using the tubular reactor/precipitator and either a needle valve, homogenizing valve, or a gear pump to maintain system pressure while removing casein and whey from the reactor. N_{Re} were laminar ($N_{Re} = 1700$) in these experiments for easier pressure control of the reactor because of the rapid buildup of protein in the line between the reactor/precipitator and the back-pressure device. No attempt was made to determine yield for these devices. The impact of back-pressure device on the largest and smallest particle sizes and average shear rates is shown in Table 2.

The needle valve was manually adjusted to maintain pressure. The homogenizing valve automatically maintained pressure to approximately ± 2000 kPa. Particles that passed through the needle and homogenizing valves were at most 45 μm . For both valves, whey preferentially exited the valve, casein would exit in spurts. Most particles were much smaller and were not sized, but their small size was caused by the

TABLE 2
Comparison of Casein Particle Size After Passed Through Various Back-pressure Devices.
 $T = 38^\circ\text{C}$, $P = 5520$ kPa, $N_{Re} = 1700$

<i>Back-pressure device</i>	<i>Largest particle size</i>	<i>Shear rate s^{-1}</i>
Needle valve	45 μm	10^3
Homogenizing valve	45 μm	10^3
Gear pump	45 μm	10^3
Moyno pump	16 mm	110 ^a
None	16 mm	—

^a Valve supplied by the manufacturer.

shearing action of the valve as it was opened and closed to maintain pressure. As either valve began to clog, some particles would burst and dissolved CO₂ was released from the particles. After a few minutes of operation, the experiments were discontinued because of a buildup of casein in the exit line and around the valve. Shear rates for the needle valve and the homogenizing valve were estimated assuming that the valve clearances were equal to the average valve opening of 0.5 cm and that valve clearances could be approximated by a circular tube:

$$\gamma = \frac{8v}{d} \quad (1)$$

where γ is the shear rate, v is the average fluid velocity, and d is the hydraulic diameter. Shear rates for both valves were on the order of 10^3 s^{-1} . The gear pump was operated in reverse and fed through the discharge end to set system pressure and remove casein and whey from the reactor. Shear rate was calculated assuming a clearance of 0.0001 m, for pump speed of 75 revolutions/min and a gear radius of 0.025 m using the approximate expression for maximum rate of shear strain given in Hoare *et al.* (1982):

$$\gamma = \frac{\pi ND}{\delta} \quad (2)$$

where N is the speed of the impeller, D is the diameter of the impeller, and δ is the gap width. Shear rate was on the order of 10^3 s^{-1} . For all devices, the abrupt pressure drop from system pressure of 5520 kPa to atmospheric was accompanied by freezing. Obviously, eqns (1) and (2) are only approximations because the true geometry of the valves and pump are not taken into account and the impact of CO₂ as pressure returns to atmospheric is not included. Even though the magnitude of shear rate is most likely greater than that reported here, the values are greater than those for the reactor and the Moyno pump, respectively, as expected. Casein particles inside the reactor were much larger than those that passed through the valve orifices or the pump. Stopping the experiment and opening the line showed that casein particles inside the reactor and exit lines were larger than those leaving the pump.

Maximum shear rate for flow through the reactor may be calculated using eqn (1) and is 170 s^{-1} .

A 12-stage progressing cavity pump, operated in reverse and fed through its outlet port, was then used to remove the casein and whey from the reactor (Tomasula, 1995). Cavities are formed inside the pump as the rotor turns within the stator. The cavities progress toward the pump discharge and simultaneously propel the particles. The manufacturer claims that each stage of the pump represents a drop of approximately 700 kPa from the preceding stage. The value of shear rate supplied by the manufacturer is only 110 s^{-1} for a gap size in the pump of 0.008 m. Maximum shear rate for flow through the reactor is on the same order. The manufacturer's value assumes no casein is caught between the rotor and stator. Hoare *et al.* (1982) showed that the fluid and precipitate (protein concentration 2.5% by weight) passing through a Mono pump experiences a maximum rate of shear strain in the gap between the rotor and the stator, causing particle breakup. Even though the Moyno passes particles as large as those found in the reactor, particle breakup was observed

as discussed below. The maximum gap size is also smaller than the largest particle size found in the reactor lines and contributes to particle breakup. A pump with a larger gap size should decrease the amount of broken particles. The Moyno pump was the most satisfactory in maintaining line pressure and the integrity of the product.

Product quality

For the tubular reactor, runs were carried out at 32, 38, 43 and 49°C, and at pressures of 5520, 6900 and 7580 kPa.

Casein prepared at 32°C and all pressures was watery. A firm product with distinct particles was obtained for all pressures and at temperatures in the range from 38 to 49°C; however, optimal product was obtained at 38°C and 5520 kPa.

Whereas casein yield was about the same under all conditions, approximately 2.8% on a dry basis, some of the casein leaving the pump at 43°C had surface damage, as indicated by a lack of distinct particles and a rubbery appearance. This damage was also observed for casein samples obtained at 38°C and 7580 kPa. At 49°C, more of the casein appeared damaged and occasionally exited the pump in the form of rubbery strips instead of friable particles. This product was similar in appearance to that of casein produced in the batch reactor at 60°C (Tomasula *et al.*, 1995). After a run at 43°C and 6900 kPa, the line between the Moyno pump and the reactor was opened. The casein remaining in the line leading to the pump did not have any surface damage and was in the form of distinct particles; however, the particles were firmer in appearance than those at 38°C. This suggests that the deformation of the protein is not a result of reaction conditions but of friction from the pump's nitrile stator to the protein. In each of the temperature runs above, the percentage of precipitated casein in whey was about 14% by weight wet basis. The solids content of casein precipitated at 5520 kPa and 38°C, 43°C, and 49°C, was 23.6%, 28.6%, and 32.8%, respectively (Tomasula *et al.*, 1995). Increasing temperature also resulted in a less friable, but firmer casein. For casein precipitated at 38°C, particle breakup occurred because of the friable nature of the casein, but the texture of the casein was such that it did not stick to the pump components. The drier casein precipitated at the higher temperatures most likely adhered to the nitrile stator or became embedded in it and then was pulled and stretched by the rotor as it turned, yielding the rubbery strips described above. The apparent frictional effects indicate that the upper limit of solids content for processing casein in the pump used in this study is approximately 29%.

The frictional effects may be alleviated by the use of a pump with a larger gap size. A stator material may also be selected to prevent sticking. However, these possibilities would necessitate a larger pump. For the same operating pressure, increasing gap size or using a more compressible stator material, means an increase in the number of stages.

HPLC results showed that the casein samples were relatively free of whey proteins, and that the whey samples were relatively free of casein proteins — an indication that fractionation of the proteins did not occur. These results are not unlike those observed in batch studies (Tomasula *et al.*, 1995).

For the spray reactor, runs were carried out at 32, 38, 43 and 49°C and at pressures of 4130 and 5520 kPa. Casein produced at 32°C and both pressures was watery. Best product was obtained at 38°C or 43°C and 4130 kPa. The reactor was

difficult to operate at 5520 kPa and no casein was obtained. The product was a bit softer in appearance and feel than that obtained in the tubular reactor. Yield averaged 2.2% on a dry basis, an indication that coagulation was incomplete.

Curd Ca content

In this study, Ca content for curd isolated in the tubular reactor (38°C, 5520 kPa, whey pH of 6.0 and curd pH of 5.8) averaged 1.4% by weight dry basis. Curd Ca contents from continuous operation are similar to those obtained in batch studies (Tomasula *et al.*, 1995), but about three times greater than that obtained by Jablonka and Munro (1985) for mineral acid precipitated curd. In addition, the curd did not have the rubbery feel of mineral acid curd precipitated at high pH and with high Ca content. In the case of the spray reactor casein, the high pH of 6.5 is indicative of incomplete precipitation. Unlike precipitation with mineral acids that leads to an almost Ca-free curd, precipitation of casein with CO₂ results in a curd where some of the micellar Ca phosphate remains with the curd. This is because of the higher precipitation pH of 5.8 as opposed to that of acid casein's 4.8.

The compositions of the casein and whey produced in this study at 38°C and 5520 kPa are compared to others as shown in Tables 3 and 4. Percentages of fat and lactic acid were not determined in this study. As shown in Table 3, protein content for CO₂-precipitated casein is within the range of that obtained for acid and rennet caseins and sodium and calcium caseinates.

Particle-size distribution studies

Results of PSD studies for casein removed from the tubular reactor and from the Moyno are shown in Fig. 4. Casein was most likely broken up in the smallest gap between rotor and stator as shown by the shift in average particle size at d_{50} from 4.8 mm to 841 μ m and the overall decrease in particle size of casein leaving the Moyno compared to that entering the Moyno. Particles <841 μ m comprise approximately 15% of the reactor casein and may be because of shearing along the reactor walls or factors related to reaction conditions (Muller & Hayes, 1962; Jablonka & Munro, 1986). Etchells (1993) recommends that pipe diameter should be 6–10 times

TABLE 3
Comparison of Caseins Produced by Various Methods With Those of this Study (All Values Converted to Dry Basis)

	Acid ^a	Rennet ^a	Sodium ^b	Calcium ^b	Tubular reactor ^c
Protein, %	96.4	90.2	95.0	94.8	93 ± 3
Ash, %	2.0	8.8	3.7	4.0	6.90 ± 0.01
Lactose, %	0.1	0.1	0.1	0.1	0.11 ± 0.01
Calcium, %	–	3.0	0.1	1.3–1.6	1.400 ± 0.004
Fat, %	1.5	0.9	1.1	1.1	–
pH	4.9	7.5	6.5–6.9	6.8–7.0	6.0

^aSouthward and Walker (1980).

^bSouthward (1985).

^c38°C and 5520 kPa.

TABLE 4
Comparison of Wheys Produced by Various Methods

	<i>Sweet whey</i> ^a	<i>pH 4.5 cottage cheese whey</i>	<i>Tubular reactor</i>
Protein, %	0.8	0.7	0.70 ± 0.05
Lactose, %	4.9	4.4	4.9 ± 0.1
Minerals, %	0.5	0.8	0.652 ± 0.008
Fat, %	0.2	0.04	—
Lactic acid, %	0.2	0.58	—
Calcium, %	0.54	1.36	0.300 ± 0.004
Moisture, %	93.4	93.6	92.700 ± 0.008
Other			1.10

^aMorr (1989)

—, not determined in this study.

the maximum particle size to avoid line blockage. Blockage of the lines was not a problem because casein is deformable and plugging or settling in the lines of the reactor was not a problem.

Results of PSD studies for curd produced in both reactors are shown in Fig. 5 and compared to batch studies. PSD studies were conducted at 4130 kPa for the spray reactor and 5520 kPa for the tubular and batch reactors. Deviations from linearity for the spray and batch reactor are most likely because of the milk-CO₂ contacting patterns used. In batch studies, CO₂ was sparged into milk. Curd particle size was generally larger for casein produced in either the spray or tubular reactors and decreased with increasing system pressure. For continuous studies, curd particle size was larger at 4100 kPa than at 6900 kPa. Although particle size is larger for the spray reactor after the casein passed through the Moyno, the spray reactor casein was less firm than casein precipitated in the tubular reactor and not as susceptible

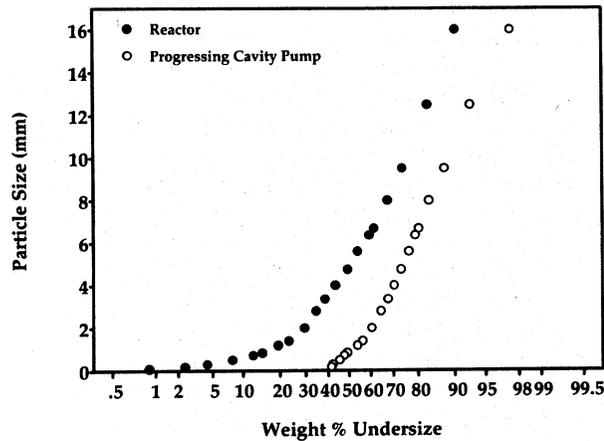


Fig. 4. A comparison of particle size distribution of casein precipitated at 38°C and 5520 kPa before and after pumping.

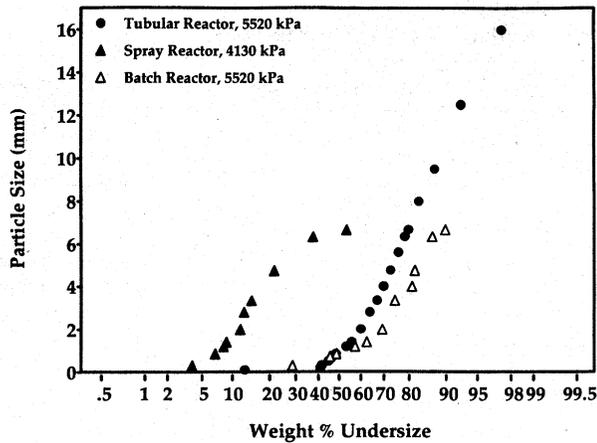


Fig. 5. Effect of CO₂-milk contacting pattern on particle size distribution of casein precipitated at 38°C.

to breakage. The largest particles were long and stringy and settled at the 6 mm sieve after slipping through the larger ones. Because pH drops with increasing pressure, these results also indicate that curd particle size increases with increasing pH, a result obtained in other studies (Jablonka & Munro, 1986).

CONCLUSIONS

Interest in technologies that present alternatives to processes that utilize strong acids or hazardous organic solvents is growing. Production of casein using CO₂ instead of mineral acids results in a casein with a high Ca content and a whey with a relatively high pH and therefore a lower mineral content than acid wheys. The continuous process presented here utilizes a pump to maintain pressure in the reactor/precipitator while allowing removal of casein and whey without disturbing system pressure or temperature. The pump is a progressing cavity pump which carries the products from the high-pressure reactor/precipitator to atmospheric conditions under lower shear conditions than a valve or gear pump. Some particle breakup was caused by the pump and some frictional damage was evident at temperatures $\geq 43^\circ\text{C}$ because the gap width of the stator/rotor assembly of the pump used in this study was smaller than approximately 60% of the particles. The continuous process shown here may be adapted for use in other processes that now use mineral acids. The pressure-reducing step alone may be used as part of a high-pressure process (pressure $< 14\,000$ kPa); e.g., in a supercritical extraction process, to continuously remove the spent solids from the process. Supercritical extraction processes are operated batch-wise with respect to the solids containing the extractable material.

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