Effect of Turbidity and Membrane Pore Size on Cross-flow Microfiltration of Apple Cider

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By: Evonne Lau
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Research Faculty Advisors:
Dr. Carmen I. Moraru
Dongjun Zhao, Ph.D. student
Department of Food Science, Cornell University

ABSTRACT

Microfiltration (MF) is a membrane separation process but its main limitation is membrane fouling. In case of apple cider MF, suspended solids (plant cell wall materials, proteins, and polyphenols) are the main contributors to fouling. In this study, the effect of turbidity, an indicator suspended solids quantity, and the membrane pore size on the flux in MF of apple cider was investigated. Raw apple cider experiments ran in a pilot-plant scale MF unit equipped with ceramic membranes of 1.4μm, 0.8μm, and 0.45μm pore sizes, varying turbidity levels, at 6°C, 5m/s crossflow velocity and 159 kPa transmembrane pressure. The permeate flux measured MF efficiency; physical-chemical properties of the cider and microfiltered juice evaluated product quality. Significant changes in pH, °Brix and viscosity were observed only for cider microfiltered with 0.45μm. At high turbidity, the 1.4μm and 0.8μm membranes resulted in similar permeate final flux (65L/m^2h), relative flux decline of 72%; while 0.45μm had the lowest final flux (37L/m^2h), relative flux decline of 55%. At low turbidity, 1.4μm, 0.8μm, and 0.45μm resulted in comparable final fluxes (49, 52, 53L/m^2h, respectively) and relative flux decline of 61%, 64%, 55%, respectively. The smallest pore size resulted in the highest rejection of particles and lowest flux, but the lowest flux decline; while the largest pore size had a higher flux, but more pronounced flux decay. This suggests that the fouling layer differs at different pore sizes. Thus, membrane pore size and pre-filtration are critical for MF efficiency and can optimize this process for commercial applications.

KEYWORDS: Microfiltration; apple cider; apple juice; membrane fouling; turbidity

INTRODUCTION

Currently, New York State juice HACCP regulations require raw apple cider to be pasteurized with a 5-log reduction of relevant pathogens to ensure food safety. In apple cider, the pathogens of concern are *E. coli* O157:H7 and the parasite *Cryptosporidium parvum* (US FDA/CFSAN, 2004). Although pasteurization is the most common method to ensure juice safety, some effects of thermal treatment, including the degradation of flavor, color, and nutritional components, affect consumer acceptability (Choi and Nielsen, 2005). Ultraviolet (UV) treatment is an alternative method for pasteurization in NY State. However, the effectiveness of this light-based treatment is limited by the turbidity of the juice / cider, due to light scattering and microbial shading effects. To increase the effectiveness of UV, membrane microfiltration (MF) can be used prior to the UV treatment to remove suspended particles. Additionally, MF will also reduce the microbial load of the cider and eliminate some of the UV resistant spoilage microorganisms.

MF is a membrane separation process able to remove particles from a fluid feed by using membranes with a nominal pore size in the range 0.05 to 2.0 μm. Current uses for MF include concentration of whey proteins, improvement in milk quality by removing microorganisms from raw milk, and clarification of vegetable and fruit juices, or of beverages such as beer and wine. Due to its energy efficiency and gentle processing on nutrition, MF has increasing applications for fruit juices in general and apple juice and cider in particular (Girard and Fukumoto 2000). Typically, the size of microorganisms in apple juice / cider range from 0.2 to 6 μm, while soluble solids, such as sugars, proteins and enzymes, are in the range of 0.005 to 0.1 μm (Girard and Fukumoto, 2010). Therefore, microorganisms (both vegetative cells and spores) from apple cider, along with some apple cider solids, are unable to pass through a MF membrane, while the

filtered juice (permeate) will retain most of its original solids, and thus, the flavor and nutritional value. Performing MF at low temperatures (cold MF) offers the opportunity to completely avoid the heating of juice and thus prevent any degradation of nutrients or flavor compounds due to heat.

As seen in previous studies, the main limitation of MF is membrane fouling, which results from adsorption and deposition of juice components, such as plant cell wall materials, proteins, and polyphenols, on the membrane surface and clogging of the membrane pores. Fouling can significantly reduce permeate flux with time, affecting processing efficiency. Among other factors, the turbidity of apple cider, which is an indicator of the concentration of suspended solids in apple cider, may relate to the propensity of the cider or juice to foul the membrane. To explain further, the suspended particles in the apple cider can adsorb onto or block the membrane pores, leading to a significant decrease of permeate flux during MF (Padilla-Zakour and McLellan, 1993).

Theoretically, the smaller the membrane pore sizes, the lower the permeate flux and the clearer the filtered apple juice. As observed by Mondor and others (1999) in the ultrafiltration of apple juice, the steady-state flux of different membrane pore sizes was governed by the fouling layer at the membrane surface, rather than the solution rejection ability of the membrane itself. The authors used mathematical models to describe flux dynamics, and defined a model parameter, A, as a measure of rates of flux decline with respect to the volume concentration factor. Thus, a small A value would signify a small flux decline (Mondor and others, 1999). In their experiments, Mondor and others determined that A increased with decreasing membrane pore size, meaning that membranes with smaller pore sizes showed a poor performance. Yet, preliminary experiments performed in our group showed that different membrane pore sizes

produced filtered juice with similar clarity. This suggests that different pore sizes of the MF membranes may lead to different membrane fouling mechanisms, but this hypothesis needs to be further explored.

In this study, the effect of turbidity on the permeate flux in apple cider MF was investigated in a pilot-scale cold cross-flow MF process. Additionally, the effect of membrane pore size on flux was investigated, since the membrane pore size relative to the size of suspended solids is also believed to play a role in formation of the fouling layer.

OBJECTIVE OF THIS WORK

The main objective of this thesis was to better understand the effect of turbidity and membrane pore size on the filterability of apple cider and chemical composition of the filtered juice. Data obtained in this work can lead to a better understanding of the mechanisms of fouling in the microfiltration of apple cider, as well as practical solutions to mitigate this problem.

MATERIALS AND METHODS

Materials

Cold, raw apple cider from Cornell Orchards (Ithaca, NY) and cold, raw apple cider from Red Jacket (Geneva, NY) were used in this work. The cider batches were stored at 4°C for a maximum of two weeks before use.

Microfiltration experiments

The pilot-scale experimental MF unit consisted of a 50 gallon feed tank connected to a variable-speed centrifugal pump, a tubular heat exchanger and a tubular ceramic membrane of Tami design (GEA Filtration, WI) placed inside a stainless steel housing (Figure 1).

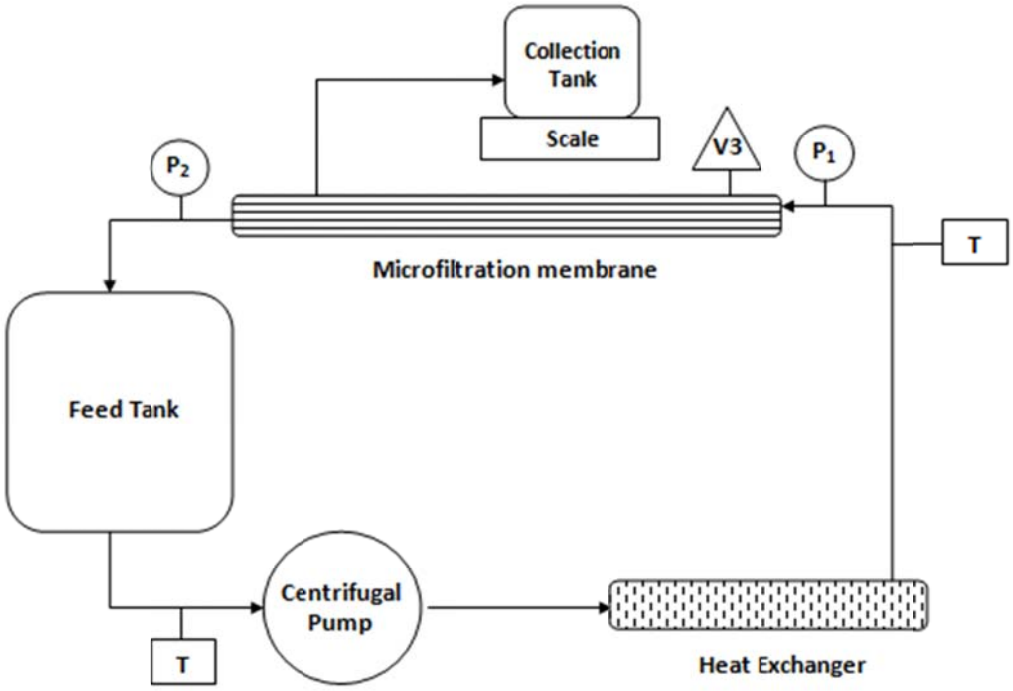


Figure 1. Microfiltration experimental setup

The membrane had an outside diameter of 25 mm, length of 1,200 mm, 23 internal channel of 3.5 mm hydraulic diameter each, and a membrane area of 0.35 m^2. Three membranes with various pore sizes were used during the experiment: 0.45 μm, 0.8 μm, and 1.4 μm, and MF experiments were performed in duplicate (n=2).

The MF processing parameters were as follows: temperature 6±1°C; cross-flow velocity: 5.0 m/s; transmembrane pressure (TMP): 159 kPa.

The transmembrane pressure was calculated using the following equation:

(1)

where P_1 is the feed inlet pressure, P_2 is the retentate outlet pressure and P_p is the permeate pressure (atmospheric pressure).

A data acquisition port was used for collecting of the temperature and pressure data. The permeate flux data was obtained gravimetrically using an electronic scale that was also connected to the data acquisition system.

The MF permeate flux (J) was calculated using the formula:

$$J = \frac{M}{A \; x \; t \; x \; \rho} \tag{2}$$

where: J: permeate flux (L/m^{2}h); M: amount of permeate (L) collected in the time interval t (hours); A: surface area of the membrane (m^2); ρ: density of the permeate at the filtration temperature (kg/m^3).

To evaluate the rate of flux decay during MF processing, a relative flux decline was calculated by dividing the value of the permeate flux at the end of the MF experiment by the initial flux. The value of the relative flux decline relates to fouling, since lower values will indicate a more pronounced fouling of the membrane. This parameter allows direct comparisons among MF experiments that have different permeate flux values. The flux decline was calculated according to the following formula:

$$Flux \;\; decline = \frac{J}{J_o} * 100, \% \tag{3}$$

where: J: permeate flux at the end of the MF experiment (after 1 hour) (L/m^{2}h); J_o: initial flux (L/m^{2}h).

Chemical cleaning of the membrane

After each MF experiment, a chemical cleaning cycle was carried out. The cleaning procedure consisted of a rinse with RO water for 10 min, followed by alkaline cleaning with Ultrasil-25 at a concentration of 20 g/L at 80°C for 30 minutes, a second RO water rinse for 10

minutes or until neutrality, acid cleaning with 5 mL/L HNO_3 at 50°C for 20 minutes, and a third RO water rinse for 10 minutes or until neutrality. The effectiveness of cleaning and change in the membrane performance with time were monitored by determining the water flux of the membrane.

MF of apple ciders with different turbidity

The turbidity of the apple cider was monitored before and after the MF process using a 2020wi turbidimeter (LaMotte Company, USA) in Formazin Nephelometric Units (FNU). MF experiments were performed on apple ciders with turbidity ranging from low to high turbidity, 600 to 800 FNU. Two MF experiments were performed in the low and high turbidity range, respectively. Due to the natural variability occurring in raw apple cider, apple cider was pre-filtered to reach the low turbidity range. To reach the desired turbidity range, raw Cornell University apple cider was blended in a 95:5 ratio with the more turbid raw Red Jacket apple cider when needed.

Chemical and Physical Analysis

pH, Brix, viscosity and particle size were measured for raw apple cider and the MF filtered juice. pH was measured at 20°C using a Fisher Scientific accumet Excel XL20 pH meter, (Fisher Scientific, Pittsburgh, PA). Brix was measured with a MISCO® digital probe refractometer (MISCO® Products Division, Cleveland, OH). Viscosity was measured at 6°C using a Brookfield DV-II+ Pro viscometer.

Particle size was measured by dynamic light scattering using a 90Plus particle analyzer (Brookhaven Instruments Corporation). Samples from each run were stored frozen and then were thawed and analyzed within three days of the experiment. Data collection and analysis was performed using the BIC software (Brookhaven Instruments Corp., Holtsville, NY), which

converted the experimental data into size distributions. Two replicate measurements were performed for each experimental condition. Each measurement consisted of 7 subsequent individual runs of 30 s duration. For each measurement, the relative particle size distribution, the intensity weighted effective diameter ( ) and the polydispersity index (p) were determined.

RESULTS AND DISCUSSION

Effect of MF on the physical-chemical characteristics of the apple cider

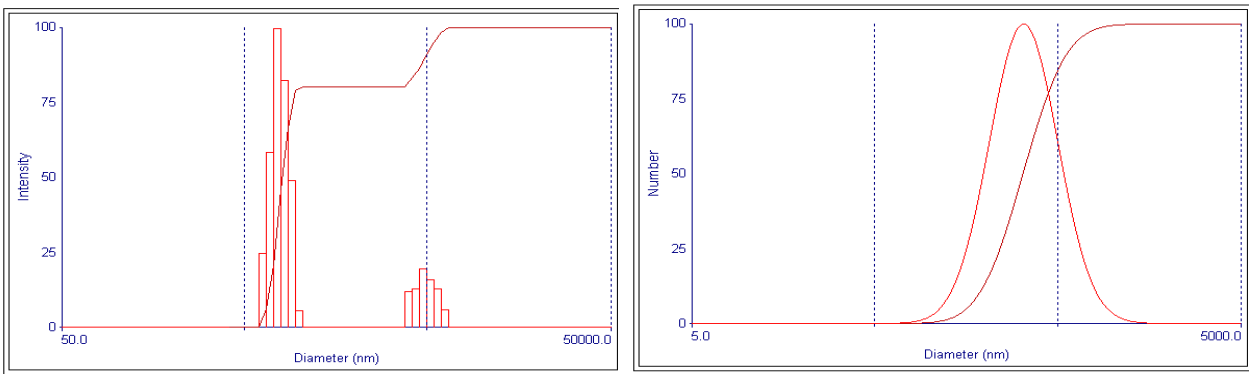
The pH, °Brix, and viscosity of the apple juice before and after microfiltration, are shown in Table 1. The most striking difference between the feed and the MF juice is the much lower turbidity of the of MF product. This is due to the retention of suspended particles from cider as a result of MF. Thus, the MF process will yield a clarified juice. Significant changes in pH, °Brix and viscosity were observed only for the apple cider microfiltered with the smallest pore size membrane, 0.45 µm.

Table 1. Average pH, °Brix, turbidity and viscosity before and after MF

MF conditions / Property	*High Turbidity Cider*			*Low Turbidity Cider*		
	0.45 µm	**0.80 µm**	**1.4 µm**	**0.45 µm**	**0.8 µm**	**1.4 µm**
pH						
Before MF (Feed)	3.37	3.49	3.61	3.37	3.64	3.70
After MF (Permeate)	3.49	3.47	3.67	3.57	3.63	3.71
°Brix						
Before MF (Feed)	12.50	12.75	12.63	12.63	13.00	12.88
After MF (Permeate)	12.75	12.88	12.88	13.00	13.38	13.25
Turbidity (FNU)						
Before MF (Feed)	791.00	804.25	780.75	682.75	750.00	705.50
After MF (Permeate)	1.57	36.93	39.63	2.40	80.10	44.05
Viscosity						
Before MF (Feed)	2.94	2.87	2.61	2.34	2.69	2.54
After MF (Permeate)	2.38	2.70	2.62	2.25	2.69	2.50

This could be due to size exclusion of the proteins, polyphenols or polysaccharides in the apple cider as a result of microfiltration. This resulted in a significant increase in the pH and decrease in the °Brix and viscosity for both the high and low turbidity ciders.

For the other two membranes, the changes in pH, °Brix and viscosity after MF were just minor. This suggests that the MF in these cases did not retain a significant amount of the soluble components from apple cider, which means that the nutritional and probably sensory



a) Multimodal particle size distribution b) Log normal particle size distribution

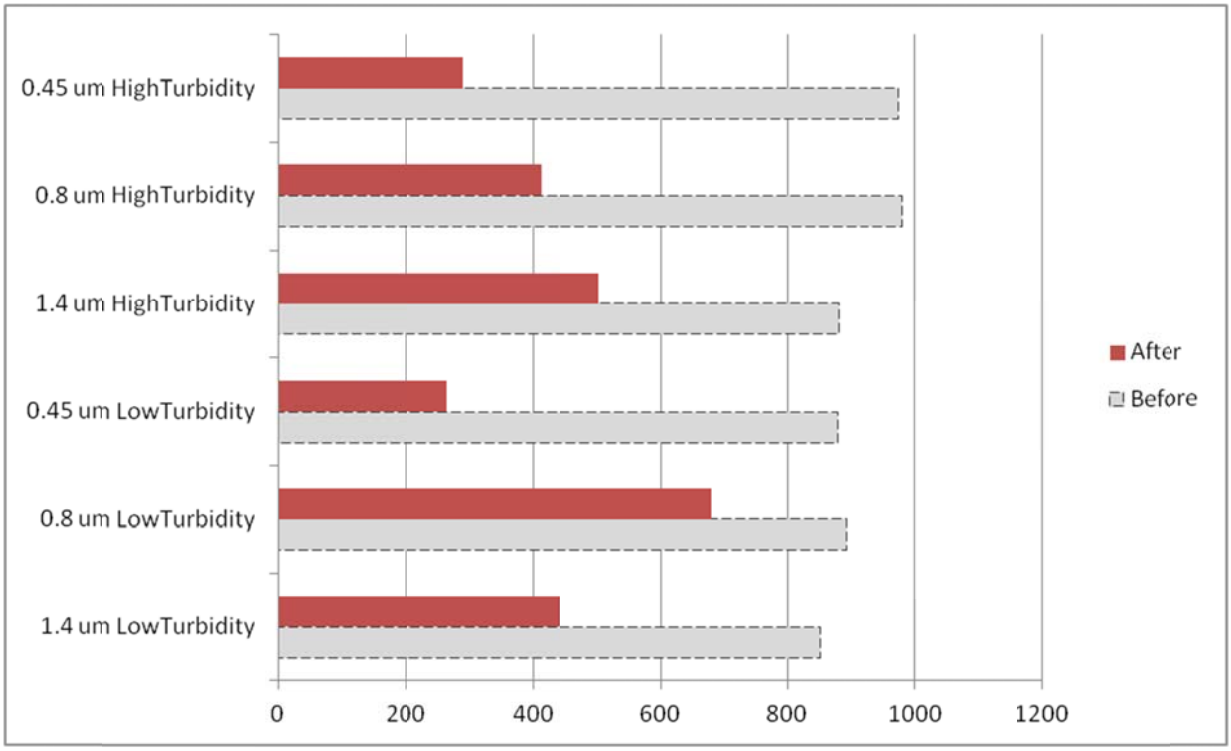
Figure 2. Graphical representation of particle size distribution in apple cider

characteristics of the final product will not be significantly altered.

The retention of suspended particles from apple cider by the membranes with different pore sizes was evaluated by conducting particle size analyses on the microfiltered product (permeate). Figure 2 shows an example of particle size distribution (PSD) data.

The results of PSD measurements can be displayed either as a multimodal size distribution (Figure 2a) or as a lognormal distribution (Figure 2b). The multimodal size distribution offers information regarding the presence of groups of particles or molecules of different sizes, but the accuracy of such representations depends greatly on the algorithms used by the specific software (Beliciu and Moraru, 2009). The lognormal distribution offers a

simplified representation of particle size distribution and is used for the calculation of a single effective diameter for the analyzed sample.



In Figure 3, the weighted average particle size values measured in the feed ("before MF") and the permeate ("after MF") for the low turbidity and high turbidity experiments are shown. Before MF, the particle sizes measured in the raw cider were similar for all ciders (908.8nm, average diameter). This suggests that the same classes of particles were present in all ciders, but their concentration was probably higher in the ciders of high turbidity as compared to those of low turbidity. After MF, the permeate obtained with 1.4µm pore size membrane, at both turbidity ranges, and the permeate from 0.8µm membrane at high turbidity had similar particle sizes (451.5nm, average diameter). The permeate from the 0.8µm membrane at low turbidity resulted

in permeates with the largest particles (diameter of 679.30nm), while the permeate from the 0.45μm membrane resulted in the smallest diameter, at both high and low turbidity (average particle diameter of 289.1 and 265nm, respectively). This apparently anomalous result could be due to different fouling mechanisms that occur in case of the low and high turbidity apple ciders, processed using the different membrane pore size membranes. In case of low turbidity apple ciders processed with 0.8μm pore size membranes, particles suspended in the cider may be larger than the size of the pores, allowing for complete retention of these particles, without significant fouling of the membrane. Meanwhile, it is possible that when processing low turbidity ciders with the 1.4μm membrane some of the submicrometric particles from the cider adsorbed onto the internal surface of the membrane pores, thus reducing the effective pore size and allowing only smaller particles to flow through. These results are consistent with the data shown in Table 1, and indicate that the membrane with a pore size of 0.45μm results in the highest reduction of apple cider particles.

Effect of the turbidity of the apple cider on the MF flux

The change in permeate flux with time during microfiltration of apple ciders of different turbidity is shown in Figures 4 and 5. Figure 4 is a compilation of the permeate flux data from high turbidity runs at 0.45, 0.8 and 1.4 μm, while Figure 5 depicts the permeate flux data from low turbidity runs at the aforementioned membrane pore sizes.

The steep decline of flux in the first moments of MF is indication of membrane fouling, which is caused by the accumulation of cider components on the membrane surface and possibly internal fouling of the pores. According to Beveridge and Wrolstad (2009) protein, polyphenols, pectin, cellulose and hemicelluloses are the components that contribute to the haze in apple cider

and juice. Pectin and protein molecules form electrostatic aggregates, increasing cloud density in cider and settling. Oxygen storage induces oxidative polymerization, forming polyphenol and cellulose-derived hazes. Arabinogalactans side chains on the pectin backbone resemble "hairs", which increases the chance for aggregation between polysaccharides and the membrane (Beveridge and Wrolstad, 2009). It is possible that these apple cider components will adsorb on the membrane surface and even block the pores, initiating fouling immediately after starting the MF process.

At high turbidity, the 1.4 µm and 0.8 µm membranes resulted in similar permeate flux values at 1 hour (~65L/m^{2}h) with a relative flux decline of 72%, while the 0.45µm membrane had the lowest permeate flux at 1 hour (~37L/m^{2}h), with a relative flux decline of 55%.

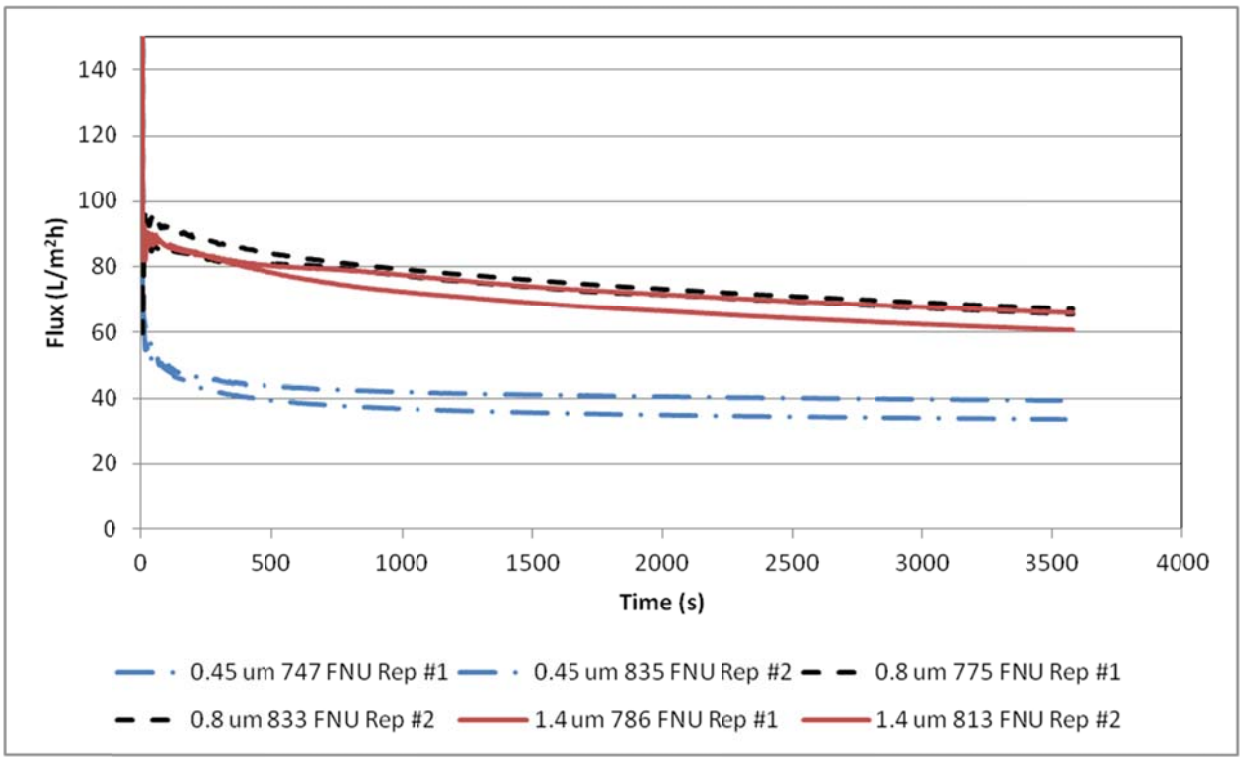


Figure 4. Permeate flux in microfiltration of raw apple cider of high turbidity

Interestingly, at low turbidity, the 1.4, 0.8, and 0.45 μm membranes resulted in comparable permeate flux values (49, 52, and 53L/m^2h, respectively, after 1 hour) and similar relative flux decline (61%, 64%, and 55%, respectively).

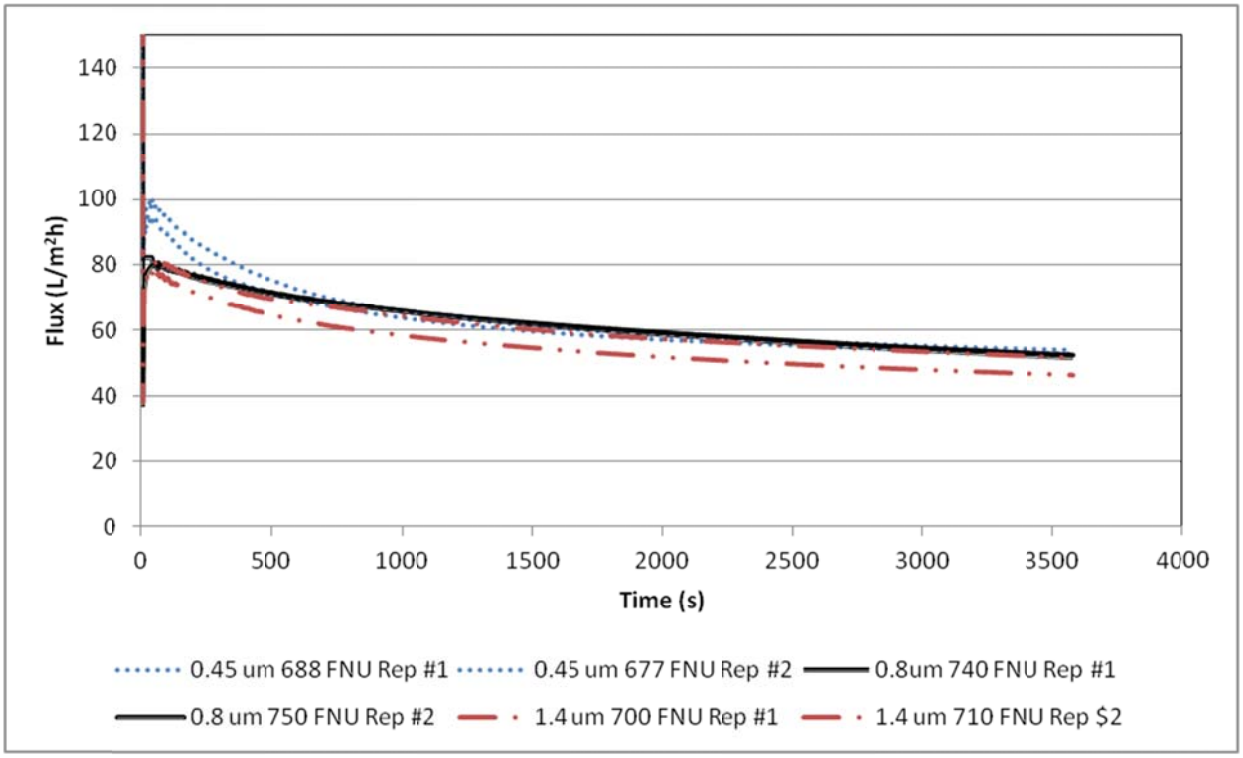


Figure 5. Permeate flux in microfiltration of raw apple cider microfiltration of low turbidity

The reduction of flux observed in all experiments is due to the membrane fouling by the components of apple cider. Adsorption of apple cider proteins, polyphenols and polysaccharides onto membrane pores reduce the size of the opening, limiting the size of the molecules that can pass through the membrane.

The fact that there was no clear correlation between permeate flux and membrane pore size (i.e. the highest pore size would yield the largest permeate flux) suggest that fouling is probably affected by the relative size of the solids in apple cider compared to the membrane pore size. In order to fully elucidate this, a larger set of data is required, and additional experiments

will need to be performed in the future. It is clear however that the fluxes obtained when microfiltering ciders with low turbidity were higher than for those with high turbidity, microfiltered under the same conditions. An explanation is that at low turbidity, the fouling layer may not have been packed as tightly as in the high turbidity, so the shear caused by the high velocity of the feed could have disrupted it, reopening up the pores and allowing the larger particles to pass through.

CONCLUSIONS

The composition of apples is subject to variability due to season and environmental factors. This, in turn, introduces variability in the composition and turbidity of apple cider and consequently in the outcome of the microfiltration process. The results of this work indicate that turbidity has an effect on the permeate flux, although more data is necessary to build a clear relationship between turbidity and flux in MF of apple cider. By understanding how turbidity relative to membrane pore size affects the permeate flux in MF, it will be possible to select the appropriate membrane pore size in order to maximize the flux permeate and thus increase processing yield.

SUGGESTIONS FOR FUTURE WORK

Although this study revealed some interesting trends, more data is needed in order to further develop and solidify the relationship between membrane pore sizes, turbidity, and fouling. Additional runs need to be performed to complete triplets for each membrane pore size. An extended turbidity range would also provide more insight on how more or less apple cider solids affect the permeate flux. Work is currently being done on this ongoing project.

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