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Defining the Proper Operating Time for the Septa Extractor

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Executive Summary

There is a desire to replace a Soxhlet Extractor, which is currently used to clean septa employed in polymerizations, with a larger automated unit called the Septa Extractor. The goals for this project were to validate the operating time of the Septa Extractor and to determine whether commercially available septa were an acceptable alternative to those prepared in-house.

In-house and commercial septa both extracted for 72 hours gave molecular weights falling inside the acceptable range. There were deviations from control samples however, in the molecular weights for these remaining two types of septa. These deviations can be attributed to several possible sources of error during the polymerizations. These include, the batch of monomer used, the seal of the reactor, and the quality of the initiator. A combination of these, most likely led to the variance in the data collected, and due to this variance, it is unclear whether the Septa Extractor can effectively clean in-house or commercial septa.

Before commissioning the Septa Extractor, it is recommended that smaller scale reactions be conducted using a new source of initiator and monomer to reduce the variability present in the current tests. These experiments should be performed using the in-house 72 hr Soxhlet Septa and both the commercial and in-house septa prepared in the Septa Extractor for 72 hr.

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Introduction

The tire and rubber industry utilizes man-made polymers, in addition to natural rubber, to manufacture tires. Synthetic rubber can be produced by means of anionic polymerizations, during which, it is important that the polymerization medium is rigorously free of reactive materials such as water, oxygen, and carbon dioxide.[1] These substances can react with polymerization species, altering the physical and chemical properties of the desired final product. During the reactions, it is necessary to charge initiators, modifiers, and other substances, into pressurized containers that are sealed with rubber septa. These septa prevent oxygen and moisture from entering the pressurized container, and the reactor, though they need to be cleaned before use to remove other impurities.

Currently a glass Soxhlet Extractor is used to remove such impurities from rubber septa. The extractor is first loaded with cyclohexane and the rubber septa. The cyclohexane is then heated with a hot plate and the vapor rises to the condenser. As the cyclohexane condenses, it drips down as a liquid onto the septa, drawing out any residue present. The liquid continues to collect until it reaches the top of the siphon, before the entire volume is drained back down to the flask. The cycle repeats for as long as the operator desires, and a diagram is shown below:

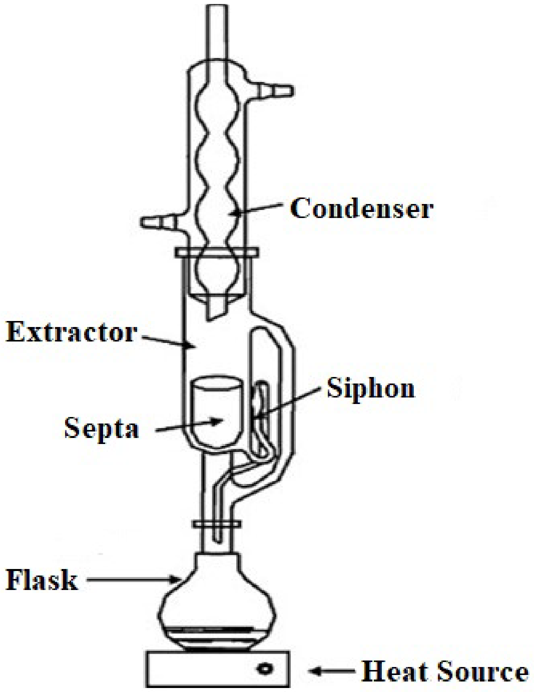

Figure 1. Model of the Soxhlet Extractor currently used to clean rubber septa.

The Soxhlet Extractor, though effective, only cleans a small number of septa at a time, so it needs to run frequently. It also needs to be kept in a hood, as a safety precaution to shield operators from exposure to cyclohexane vapor. These limitations led to the commissioning of the Septa Extractor, which is an automated process unit designed to perform the same function as the Soxhlet Extractor, on a larger scale. A diagram for the Septa Extractor is shown below:

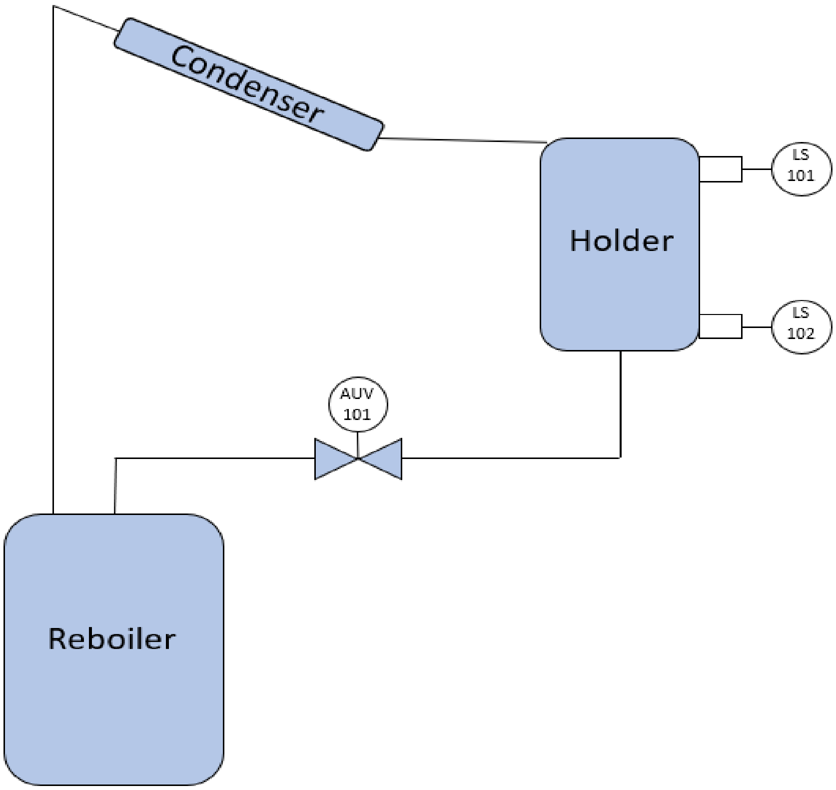

Figure 2. A basic diagram of the Septa Extractor. Septa are loaded into a basket inside the Holder, and cyclohexane is transferred to the Reboiler. As the cyclohexane is heated, vapor travels through the Condenser, and warm liquid rains down on the septa inside the basket. Once the upper-level switch (LS 101) is tripped, an automated valve (AUV 101) is opened, and the Holder drains until the liquid level falls below the bottom level switch (LS 102). AUV 101 then closes and the cycle repeats for as long as the operator desires.

Therefore, the primary goal of this project is to determine the operating time required to effectively clean the rubber septa by extraction. In addition, currently, the septa are compounded in-house, and are cut individually by an operator. It can take multiple days for an operator to cut enough septa to fill and run the Septa Extractor, which is time spent away from other forms of work. Hence, the secondary goal of the project is to determine whether a commercially available alternative can replace the in-house septa to save on labor costs.

Tables 1 and **2** summarize all the septa to be evaluated in the project. The septa, either obtained commercially or prepared in-house, were cleaned as indicated in the table. A standard anionic polymerization of butadiene will be used to assess the differences between six types of septa used to seal the pressurized containers. Three pressurized containers were used for each reaction, one to charge the modifier, one to charge the initiator, and one to collect a conversion sample during the reaction.

Table 1. A summary of the six types of septa that will be analyzed throughout the project. Two types of control septa: commercial before extraction and in-house purified in the Soxhlet Extractor for 72 hours, will serve as standards to show the importance of the removal of impurities.

Experiment No.	Type of Septa	Septa Extractor Run Time (hrs)
1 (standard)	In-House	72 – Soxhlet Extractor
2	Commercial	Control
3	In-House	48
4	In-House	72
5	Commercial	48
6	Commercial	72

Table 2. A summary of the validation batches that will be analyzed to determine the difference between the commercial and in-house septa.

Experiment No.	Type of Septa	Septa Extractor Run Time (hrs)
7 (standard)	In-House	72 – Soxhlet Extractor
8	In-House	72 – Soxhlet Extractor
9	In-House	72 – Soxhlet Extractor
10	Commercial	72
11	Commercial	72
12	Commercial	72

Gel Permeation Chromatography (GPC) was used to determine the peak molecular weight (Mp), the number-average molecular weight (Mn), and weight-average molecular weight (Mw) of each sample. For each set of experiments, the Mp from each batch will be compared to a corresponding experimental standard (Batch 1in **Table 1** and Batch 7 in **Table 2**). Since molecular weight increases as the amount of active initiator decreases, which is caused by the presence of impurities, deviations greater than 10% in the Mp will indicate the presence of impurities remaining in the septa.[2]

Nuclear Magnetic Resonance (NMR) was used to determine the vinyl content of each sample. Conversion was also determined by dividing the experimental solids by the targeted total solids, with measurements recorded in **Appendix A** and sample calculations shown in **Appendix B**. The polydispersity indices (PDI) were calculated for each sample (with sample calculations shown in **Appendix B**) and were compared to the expected PDI for anionic polymerizations, which is typically less than 1.1.[2] The Mp, PDI, vinyl content of the product, and the conversion of the monomer were compared to determine the importance of impurity removal from the septa and the optimal extraction approach.

Experimental Methods

Septa Preparation

Septa (either the in-house or the commercial alternative) were first loaded into basket inside the Holder, with 10 marked as measurement samples. After the septa were loaded, the Holder was sealed, and the desired amount of cyclohexane was charged to the Reboiler. The unit was then vented down to prevent nitrogen blinding from occurring in the Condenser during operation.

The appropriate utilities were turned on for the Reboiler and the Condenser, and the unit was monitored by an operator for about one hour to ensure proper cycling was occurring. The unit was then allowed to run for an additional 24 hours, before being shutdown to perform sample septa measurements. The sample septa were removed and measured every 24 hours to observe the changes in their diameter and thickness. These measurements can be found in **Appendix C.** An additional quantity of septa, about 10, were removed after 48 and 72 hours of operation and set aside to perform the experiments listed in **Tables 1** and **2**.

After being removed from the Septa Extractor, the measurement samples and the septa reserved for batches, were dried in a vacuum oven at 80°C for four and a half hours.

Polymer Synthesis

Polymers were produced in 10-pound batches, with solvent, monomer, initiator, and modifier quantities determined based on a target vinyl content of 15%, a target total solids of 15%, and a target molecular weight of 170 kg/mol.

Pressurized containers were sealed with the corresponding septa and purged with nitrogen for 3-4 hours before each batch. The batch solvent was then measured and charged to the reactor. The monomer was then measured and charged to the reactor. The pressurized containers were then prepared by adding the desired amounts of modifier, initiator, or terminator. The agitator was turned on, and the modifier container was first charged in the reactor followed by the initiator.

Both containers were rinsed with solvent, that was charged into the reactor as well, to ensure that minimal modifier and initiator were lost. The reactor jacket temperature was then set to 145°F to begin the polymerization.

The reaction was monitored until it reached a peak exotherm temperature, and about 15 minutes after that point, the conversion sample was collected from the reactor. The sample was removed from the container and weighed before being placed in an oven to dry. After about 30 minutes, its dried weight was obtained and recorded. After the collection of the conversion sample, the agitator and jacket heating system were turned off. The system was allowed to cool below 140°F before the polymer cement was dropped into a bucket with terminator solution. The cement was processed in a drum dryer to remove the remaining solvent, before being submitted for analytical testing. The reactor was cleaned between each batch with fresh solvent and a small amount of initiator.

Data & Results

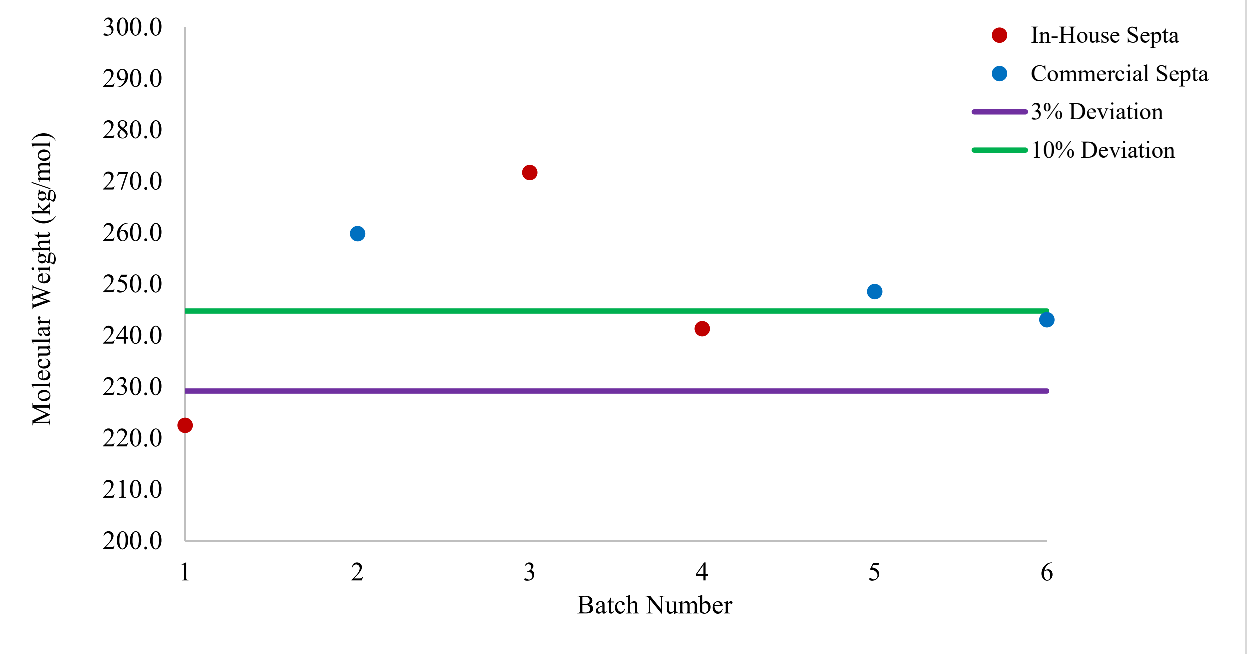

Figure 3. The Mp (kg/mol) of the polymer for each of the corresponding batches in **Table 1**. The deviation lines correspond to a 3% and a 10% deviation of the Mp for Batch 1.

As seen in **Figure 3** above, only Batches 4 and 6 fell within the acceptable Mp deviation from batch one. Batches 2, 3, and 5 were all above the 10% deviation line, suggesting that commercial septa before extraction, the in-house septa extracted for 48 hours, and the commercial septa extracted for 48 hours all still contain impurities.

Table 3. The vinyl content, monomer conversion, molecular weights, and PDI for the polymers produced using each type of septa listed in **Table 1**.

Batch	**Septa Used**	**Vinyl Content**	**Conversion**	**Mp (kg/mol)**	**Mn (kg/mol)**	**Mw (kg/mol)**	**PDI**
1	In-House 72 hr Soxhlet	13.8%	92.9%	222.5	222.6	242.6	1.09
2	Commercial Before Extraction	13.8%	90.7%	259.9	260.9	281.0	1.08
3	In-House 48 hr Septa Extractor	13.5%	89.5%	271.7	273.3	291.2	1.07
4	In-House 72 hr Septa Extractor	13.7%	78.7%	241.3	241.2	260.1	1.08
5	Commercial 48 hr Septa Extractor	12.4%	80.5%	248.6	250.5	266.5	1.06
6	Commercial 72 hr Septa Extractor	13.0%	73.5%	243.1	244.9	263.0	1.07

As shown in **Table 3** above, the PDI for Batches 1 through 6 fell below the expected PDI for a typical anionic polymerization. The vinyl contents, though slightly off from the expected 15%, did not deviate much from each other, only having a standard deviation of ±0.52%.

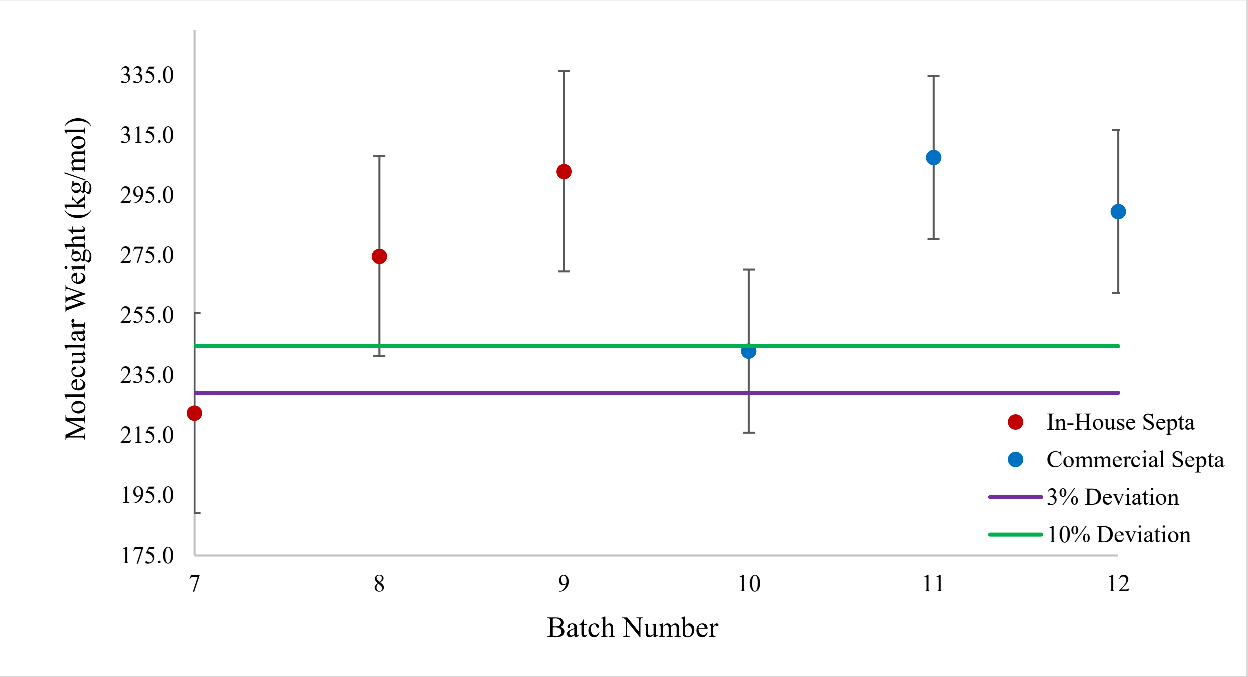

Figure 4. The Mp (kg/mol) for each of the corresponding batches in **Table 2.** Error bars were determined using one standard deviation of the in-house and commercial Mps, which were ± 33.3 kg/mol and ± 27.2 kg/mol, respectively. The deviation lines correspond to a 3% and a 10% deviation of the Mp for Batch 7.

As seen in **Figure 4** above, only Batch 10 fell within the acceptable Mp deviation from the standard. However, when comparing the averages of the in-house and commercial septa, which were 266.8 kg/mol and 280.1 kg/mol, respectively, there is only about a 5% difference between their performance. This 5% deviation would suggest that the Septa Extractor can prepare septa that are suitable for use in polymerizations. However, it should be noted that the standard deviations for both sets of septa were somewhat large, and this degree of variability is undesirable. This variance present across the data sets, is not necessarily due to impurities present in the septa. Impurities in the polymerization might have been introduced through other sources of error. These possible errors include, the batch of monomer used (a different source was used for experiments 7 through 12 than that in Batches 1 through 6). The seal of the reactor was another potential source of error, since a leak was discovered during experiments 7 through 12, that was not present in the first set, which could have introduced moisture and/or oxygen into the reactor. The initiator used also likely could have introduced moisture and/or oxygen into the reactions, since it was noticed during experiments 7 through 12 that the initiator container was not sealing properly.

Table 4. The vinyl content, monomer conversion, molecular weights, and PDI for the polymer produced using each type of septa listed in **Table 2**.

Batch	Septa Used	Vinyl Content	Conversion	Mp (kg/mol)	Mn (kg/mol)	Mw (kg/mol)	PDI
7	In-House 72 hr Soxhlet	13.8%	92.9%	222.5	222.6	242.6	1.09
8	In-House 72 hr Soxhlet	12.1%	93.0%	274.7	268.9	289.7	1.08
9	In-House 72 hr Soxhlet	12.1%	99.2%	303.0	307.6	341.8	1.11
10	Commercial 72 hr Septa Extractor	13.0%	73.5%	243.1	244.9	263.0	1.07
11	Commercial 72 hr Septa Extractor	11.9%	72.1%	307.6	305.4	346.9	1.14
12	Commercial 72 hr Septa Extractor	12.1%	87.0%	289.6	292.6	324.1	1.11

As shown in **Table 4** above, the PDI for Batches 7, 8, and 10 fell below the expected PDI for a typical anionic polymerization, with the PDI for Batches 9, 11, and 12 being slightly greater than the expected PDI for an anionic polymerization. The vinyl contents for each batch, though off from the expected 15%, did not deviate much from each other, only having a standard deviation of ±0.69%. However, it is worth noting they deviated further from the expected 15% than those in Batches 1 through 6.

Conclusion & Recommendations

It appears possible that the in-house or commercial septa prepared in the Septa Extractor for 72 hr may be suitable in polymerizations. However, it is recommended that additional data be collected for both types of septa before commissioning the Septa Extractor, with the intent to minimize the errors found in reactions 7 through 12.

The deviations found in the Mp, vinyl content, and PDI for Batches 8 through 12 can be attributed to several possible sources of error during the polymerizations. These include, the batch of monomer used, the seal of the reactor, and the quality of the initiator. A combination of these, most likely led to the variance of the Mps for Batches 7 through 12, and due to this variance, it is unclear whether the Septa Extractor can effectively clean in-house or commercial septa.

If possible, it is recommended that smaller scale reactions be conducted to eliminate the error present in the reactor seal. A new and unused source of initiator should be used in this experiment, along with the same batch of monomer, to eliminate those sources of error as well. These experiments should be performed using the in-house 72 hr Soxhlet Septa and the commercial and in-house septa prepared in the Septa Extractor that were both cleaned for 72 hr. The 72 hr Septa Extractor commercial and in-house septa should be used, since they were the only septa that fell within the acceptable Mp deviation (as seen in Batches 4 and 6).

Between 3 and 6 reactions for each type of septa should be conducted at this smaller scale, with the all the Mps being analyzed and compared to each other. If the Mps for either the commercial or in-house septa are comparable (i.e., fall within the acceptable Mp deviation from the in-house septa prepared in the Soxhlet Extractor) then the Septa Extractor can be commissioned to replace the Soxhlet Extractor.

References

[1] R. J. Young and P. A. Lovell, Introduction to Polymers, 2nd ed., London: Chapman & Hall, 1991.

[2] P. C. HIemenz and T. P. Lodge, Polymer Chemistry, 2nd ed., Boca Raton, Florida: CRC Press, 2007.

Appendix A: Conversion Measurement Data

Table 5. The cement and polymer weights determined by performing a total solids test on each batch. The actual percent solids, along with the total monomer conversion were determined from these total solids tests.

Batch No.	Cement Weight (g)	Polymer Weight (g)	Actual % Solids	Conversion
1	1.198	0.167	13.9%	92.9%
2	1.263	0.172	13.6%	90.8%
3	1.318	0.177	13.4%	89.5%
4	1.310	0.154	11.8%	78.4%
5	1.267	0.153	12.1%	80.5%
6	1.334	0.147	11.0%	73.5%
7	1.198	0.167	13.9%	92.9%
8	1.312	0.183	13.9%	93.0%
9	1.338	0.199	14.9%	99.2%
10	1.334	0.147	11.0%	73.5%
11	1.249	0.135	10.8%	72.1%
12	1.302	0.170	13.1%	87.0%

Appendix B: Sample Calculations

Monomer Conversion

To determine the monomer conversion in each batch, the actual percent solids first needed to be determined:

$$actual\ \%\ solids = \frac{polymer\ weight}{cement\ weight} * 100\%$$

The polymer weight and cement weight were obtained from the conversion sample taken during each batch. When the polymer weight is 0.167 g, and the cement weight is 1.198 g the actual % solids is:

$$actual\ \%\ solids = \frac{0.167\ g}{1.198\ g} * 100\%$$

$$actual\ \%\ solids = 13.9\%$$

The actual percent solids, along with the expected percent solids of 15%, could then be used to determine the monomer conversion:

$$X = \frac{actual\ \%\ solids}{expected\ \%\ solids} * 100\%$$

$$X = \frac{13.9\%}{15.0\%} * 100\%$$

$$X = 92.7\%$$

PDI

To determine PDI for each sample, the Mn and the Mw weight were obtained from GPC analysis of each polymer batch.

$$PDI = \frac{Mw}{Mn}$$

For batch one, which had a Mn of 222628 g/mol and a Mw of 242577 g/mol the PDI was determined using the following:

$$PDI = \frac{242{,}577\ g/mol}{222{,}628\ g/mol}$$

$$PDI = 1.09$$

Appendix C: Septa Thickness and Diameter

Table 6. The thickness and diameter of the in-house septa measured at 24-hour increments throughout the Septa Extractor run. It should be noted septa 7 was lost between the initial measurement period and the 24-hour mark measurement.

	Initial		After 24 hrs		After 48 hrs		After 72 hrs		After Drying	
Septa	**Thickness (mm)**	**Diameter (mm)**	**Thickness (mm)**	**Diameter (mm)**	**Thickness (mm)**	**Diameter (mm)**	**Thickness (mm)**	**Diameter (mm)**	**Thickness (mm)**	**Diameter (mm)**
1	1.91	25.45	1.97	27.05	1.97	27.30	1.86	26.57	1.93	25.76
2	1.88	25.45	1.97	27.10	1.93		1.84	26.73	1.84	25.73
3	1.93	25.45	1.94	27.06	1.94		1.91	26.31	1.88	25.80
4	1.88	25.45	1.95	27.09	1.96		1.89	26.46	1.85	25.93
5	1.88	25.45	1.88	27.10	1.92	27.27	1.81	26.95	1.83	25.80
6	1.80	25.45	1.89	27.11	1.97	27.21	1.77	26.83	1.75	25.64
7	1.90	25.45								
8	1.89	25.45	1.91	27.03	1.96	27.29	1.89	26.97	1.86	25.75
9	1.93	25.45	1.94	27.04	1.94		1.90	26.75	1.87	25.75
10	1.90	25.45	1.96	27.08	1.96		1.88	26.73	1.85	25.58

Table 7. The thickness and diameter of the commercial septa measured at 24-hour increments throughout the Septa Extractor run.

	Initial		After 48 hrs		After 72 hrs		After Drying	
Septa	**Thickness (mm)**	**Diameter (mm)**	**Thickness (mm)**	**Diameter (mm)**	**Thickness (mm)**	**Diameter (mm)**	**Thickness (mm)**	**Diameter (mm)**
1	1.58	25.60	1.58	25.85	1.58	25.63	1.54	24.57
2	1.55	25.61	1.62	26.08	1.58	25.93	1.55	24.81
3	1.52	25.79	1.58	26.05	1.58	25.95	1.53	24.80
4	1.54	25.63	1.58	25.86	1.56	25.79	1.52	24.62
5	1.54	25.63	1.58	26.01	1.57	25.81	1.56	24.65
6	1.51	25.73	1.55	25.84	1.51	25.69	1.51	24.56
7	1.54	25.62	1.56	26.08	1.54	25.93	1.52	24.40
8	1.57	25.63	1.56	26.23	1.55	25.90	1.54	24.45
9	1.58	25.53	1.60	26.10	1.63	25.43	1.58	24.56
10	1.52	25.52	1.55	26.27	1.56	25.89	1.53	24.58