

FINAL REPORT

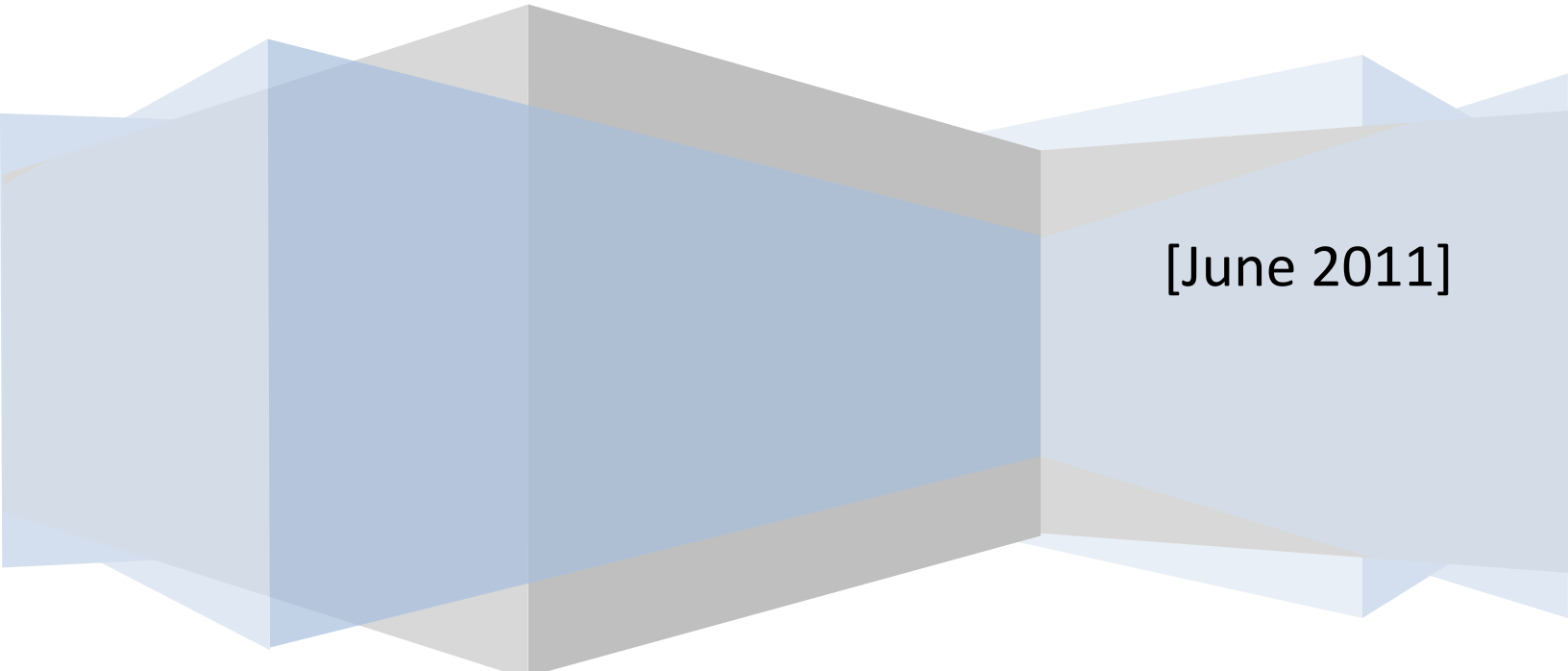
Separation of Ethanol- Water Mixtures Using Canola Meals

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[June 2011]

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Separation of Ethanol-Water Mixtures Using Canola Meals
June 2011

SCDC and PMI Awards

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1. Summary

Through the project, canola meal biosorbents were successfully made in the forms of particles, and cylindrical pellets. The biosorbent pellets enhanced the stability of canola meal material. Characterization of the biosorbents was done by measuring the surface area. Two lab-scale adsorption column systems were established in the laboratory of the University of Saskatchewan to optimize the performance of the canola meal biosorbents for ethanol dehydration. One is a fixed-bed water adsorption system consisting of a vaporizer, a stainless steel dehydration column packed with the canola meal particles, a condenser and a product collector. Through this process, the biosorbents particles were able to dry ethanol vapour with 4 to 90 wt% water content to achieve over 99 wt% ethanol. The column temperature was optimized at 85°C. The other one is a Pressure Swing Adsorption (PSA) process which mimics the PSA process in bioethanol plants. The process has successfully used the canola meal cylindrical pellets to dry 50wt% - 95wt% ethanol and obtain 97.9 wt% - 99.6 wt% ethanol. The important parameters affecting the dehydration were investigated including pressure of 18-22psi, ethanol feed concentration 5-95wt%, dehydration column temperature 85-105°C and feed flowrate 5-9ml/min. It has been demonstrated through a central composite design that there is interaction between the column temperature, pressure, and feed flowrate and concentration, from which a model was generated. The water saturated canola meal pellets were able to be regenerated online by purging nitrogen under vacuum or offline oven dried at 105°C. They have been reused in the lab for over a year without deteriorated quality.

In addition, it was investigated that the nutrients originally contained in the canola meal including minerals and proteins did not change significantly in the canola meal pellets after used in ethanol dehydration for over a year. Furthermore, it was demonstrated that water uptake from liquid phase was increased by canola meal after protein extraction using alkali method compared with raw canola meal. The higher the concentration of sodium hydroxide used to extract protein, the higher the water uptake. The results show the great potential of canola meal after protein extraction for ethanol dehydration.

Research through this project shows canola meal has a great potential for dehydration of bioethanol, and other alcohols and gases.

This final report summarized the important research results achieved from the start of the project through May 30, 2011, addressed the challenges encountered in the project and proposed the future work.

2. Background

The goal of this proposed research is to develop a process for effectively dehydrating ethanol from ethanol-water mixtures. Research into this process is important. There is increasing

interest in using bioethanol as a sustainable energy source. The conversion of carbohydrates to bioethanol through fermentation generally leads to a broth that contains 5-12 wt% of ethanol mixed with water and some other organics. In the ethanol industry, the recovery of ethanol from the fermentation broth to fuel grade is mainly by distillation of fermentation strength ethanol to 95 wt% ethanol-water mixture below the azeotrope (95.6 wt% ethanol), followed by adsorption using molecular sieves to remove the remaining water. However, the commercial 3A-molecular sieves suitable for bioethanol dehydration have water uptake lower than 0.25 g/g dry adsorbent (Simo, et al. 2009; Carmo and Dubulin, 2006), which limits the molecular sieves to be applicable for drying a 95wt% ethanol-water mixture. In addition, the temperature for drying molecular sieves is high up to 190-210°C. Cost effective cellulose and starch based adsorbents have a potential for drying ethanol. It was reported that corn grit has been used to dry ethanol in ethanol industry (Ladisch, et al. 1984). However, use of corn places pressure on food consumption. There is therefore an incentive to develop an alternative process for ethanol dehydration.

According to Statistic Canada, prairie farmers expect canola production will increase 10.9% to a record 13.0 million tonnes in the year of 2011. In Saskatchewan, farmers anticipate a potential record production of 6.5 million tonnes. A large amount of canola meal is produced in the canola industries including oil extraction and biodiesel production. The commercial price of canola meal is about \$0.30 /kg in the year of 2011, much cheaper than that of molecular sieves (\$3~4/kg). In our preliminary research, we have determined that water uptake by canola meal reached 2.1 kg water /kg dry canola meal, while that by molecular sieves is lower than 0.25 kg/kg dry adsorbent. The molar uptake of liquid ethanol by canola meal is 9 times lower than that of water. We have also demonstrated that ethanol can be concentrated by feeding 10-95% ethanol water vapor into a column packed with canola meal. However, to commercialize the technology, further research work needs to be done on formulation of canola meal adsorbent with high performance and low costs for ethanol dehydration.

The ultimate goal of the research is to generate a technology to make new use of canola meal as adsorbent for ethanol drying and reduce the costs of ethanol production. It is recognized in the ethanol industry that reducing the costs for ethanol dehydration will greatly decrease production costs and enhance the international competitiveness of the industry. On the other hand, the Saskatchewan agricultural and other relevant industries are expected to enhance their profit by selling their waste canola meals. Additionally, increased supply of ethanol will benefit the environment. The timeframe for these benefits will be the next decade, but the benefits should be ongoing and cumulative into the far future. To that end, the following objectives were proposed in this project.

3. Overall Objectives of the Project

The aim of the project is to develop cost-effective bio-sorbents from canola meals to selectively remove water from the ethanol-water mixtures so as to obtain fuel grade or anhydrous ethanol. To that end, the sub-objectives of the project were proposed as follows:

- Develop and characterize biosorbents made from canola meals.
- Optimize the conditions for selective water uptake in ethanol-water mixtures using the biosorbents.
- Establish an adsorption column system capable of drying ethanol with a range of water contents to obtain fuel grade and anhydrous ethanol.

4. Methodology and results achieved through this project

4.1 Biosorbent formulation (Phase I of the original research plan)

4.1.1 Biosorbent particles

Biosorbent particles were prepared by sieving the canola meal (Co-op Feeds), giving sizes of < 0.45 mm, 0.425 mm - 1.18 mm, and 1.18 mm - 3.35 mm. The particles were oven dried at 105°C. For tests in the fixed-bed adsorption system, the particles size was 0.25 mm - 1.18 mm. The biosorbents were characterized by a surface area analyzer (Micromeritics ASAP 2020). The BET surface area was 1.9 m²/g for particle sizes less than < 0.425 mm, slightly decreased to 1.8 m²/g for sizes of 0.425 mm - 1.18 mm and significantly reduced to 0.35 m²/g for sizes of 1.18 mm - 3.35 mm.

4.1.2 Canola meal cylindrical pellets

In order for industrial application, canola meal particles are preferably made into pellets with enhanced stability, re-usability and ease of operation. We successfully made the pellets in pilot scale from the canola meal particles (Co-op Feeds) using a California Pellet Mill (CPM-Laboratory Model CL-5, California Pellet Mill Co., Crawfordsville, IN). The pellets are in a uniform size of about 5 mm in diameter and 2.5 mm in length.

The pellets enhanced the stability of the canola meal particles. They were used continuously in a Pressure Swing Adsorption process established in the lab to simulate commercial ethanol dehydration process for four months in 2010 and are still available to use without deteriorated quality. Figure 1a shows the raw canola meal particles and Figure 1b shows the pellets after used for one year.

The surface area was reduced after canola meal particles were made into pellets. To overcome this, we increased the surface area of the pellets by addition of water to the pellets with ratios of 0.1-0.6 g water /g dry canola meal in the pellet making process. After being made, the pellets were oven-dried at 105°C and then used for ethanol dehydration.

We also found that the addition of starch to the canola meal together with water in the pellet-making process can enhance the surface area of the pellets.



a. Raw canola meal particles

b. Canola meal pellets

5 mm in diameter and 3 mm in thickness

Figure 1. Canola meal biosorbents

In the original research plan, we also intended to test greenseed canola meal. We have contacted local industry for green seed canola meal such as Milligan Bio-Tech Inc., but have not received the green seed meal. Limitation of the availability of such meal may indicate that test of greenseed canola meal may not be practical.

4.2. Optimization of selective water uptake by the biosorbents (Phase II)

4.2.1 Adsorption kinetics and equilibrium

This part of work was done by using canola meal particles in water and/or ethanol liquid in a batch stirred tank. The time required to reach water/ethanol adsorption equilibrium was affected by particle size of canola meal, mixing speed, and temperature. The smaller the size of the canola meal particles, the faster the adsorption. We also demonstrated that the higher the mixing speed in the range of 0-280 rpm, the faster the adsorption. Increasing temperature from 5°C to 60°C, water adsorption was increased at first 30 min (Figure 2). However, at equilibrium, maximum water uptake was achieved at 25°C. The water uptake decreased as follows: 25°C > 40°C > 60°C > 5°C, indicating the water uptake at 25 °C - 60°C may be exothermic and physical adsorption. All of them reached equilibrium within 2 hr.

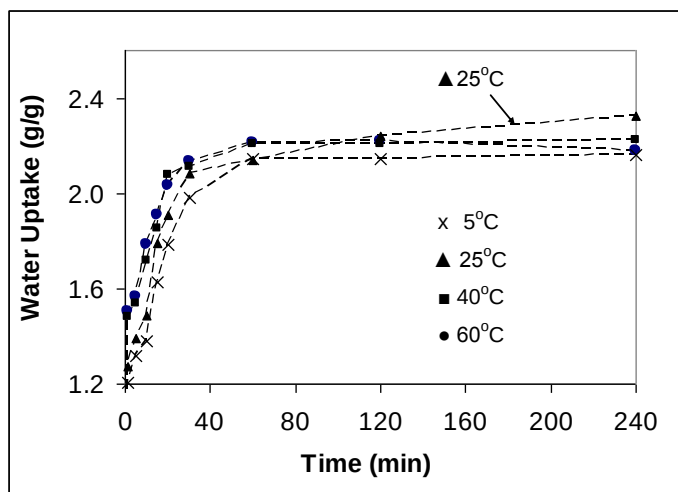


Figure 2. Effect of temperature on water uptake. Each sample containing 4 g canola meal powder (1.18 mm - 3.35 mm) and 150g 100% water was run at a mixing speed of 130 rpm.

Figure 3 shows the effect of temperature on ethanol uptake. Similarly, increasing temperature increases the ethanol uptake at the first 30 min. However, equilibrium ethanol uptake almost reached the same value at 25°C, 40°C, and 60°C, with the lowest value at 5°C. It was determined that the water adsorption by particles (1.18 mm -3.3.5 mm) at 25°C and 130rpm achieved 90% of the equilibrium uptake at the first 30 min and reached equilibrium at about 2 hr

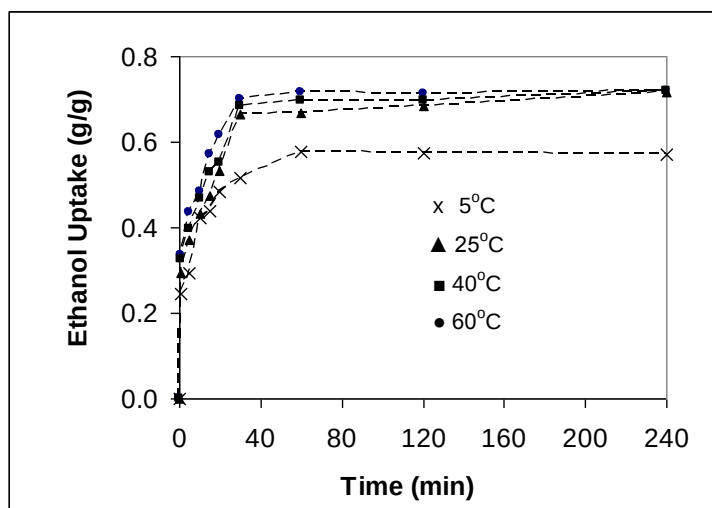


Figure 3. Effect of temperature on ethanol uptake. Each sample containing 4 g canola meal powder (1.18 mm - 3.35 mm) and 150g 100% ethanol was run at a mixing speed of 130 rpm.

with uptake of $2.33 \pm 0.12 \text{ g/g}$. Under the same condition, ethanol adsorption also achieved 92% of the equilibrium uptake at the first 30 min and reached equilibrium at about 2 hr but with a much lower uptake of $0.72 \pm 0.05 \text{ g/g}$. Since over 90% of the equilibrium uptake was achieved for water and ethanol at 30 min, effect of water concentration on water or ethanol uptake were investigated at 30 min.

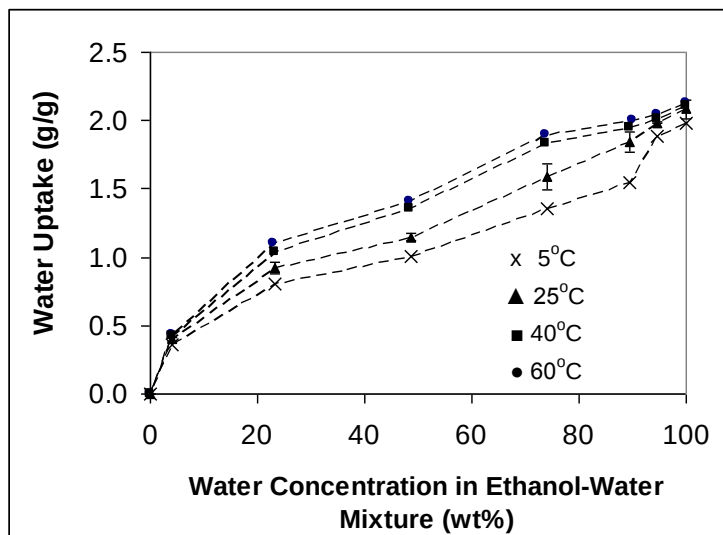


Figure 4. Effect of water concentration on water uptake. Each sample containing 4 g canola meal powder (1.18 mm - 3.35 mm) and 150 g solution was run at a mixing speed of 130 rpm for 30 min.

As shown in Figure 4, water uptake by canola meal particles increased as water concentration in the ethanol-water mixture was increased. This shows canola meal biosorbent is able to adsorb water from ethanol water mixture with a wide water concentration range (4 wt% - 100wt%). In addition, the uptake increased as temperature was increased from 5°C to 60°C when the contact time is at 30 min. Compared with commercial 3A molecular sieves used for liquid water or ethanol adsorption, the water uptake is constantly higher in the all the tested range (Carmo and Gubulin, 2006).

Figure 5 shows canola meal particles are also able to adsorb ethanol in the mixture containing 5.3wt% - 100wt% ethanol. However, the maximum ethanol uptake (0.68 g/g) is much lower than that of water (2.13g/g).

The achieved maximum equilibrium water uptake of 2.33 ± 0.12 g/g dry canola meal in this work is much higher than that of the 3A molecular sieves (MS) (0.18-0.25g water/g MS) (Simo, et. al., 2009; Carmo and Dubulin, 2006) often used in industrial ethanol dehydration process. The maximum ethanol uptake obtained at temperatures of 5-60°C was 0.72 ± 0.05 g/g dry canola meal which is higher than that by molecular sieves 0.001g/g (Simo, et al., 2009). The results demonstrated that biosorbents made from canola meal have a potential for selectively removing water from ethanol-water mixture, however, further optimization of canola meal adsorbents could be made to enhance the water selectivity.

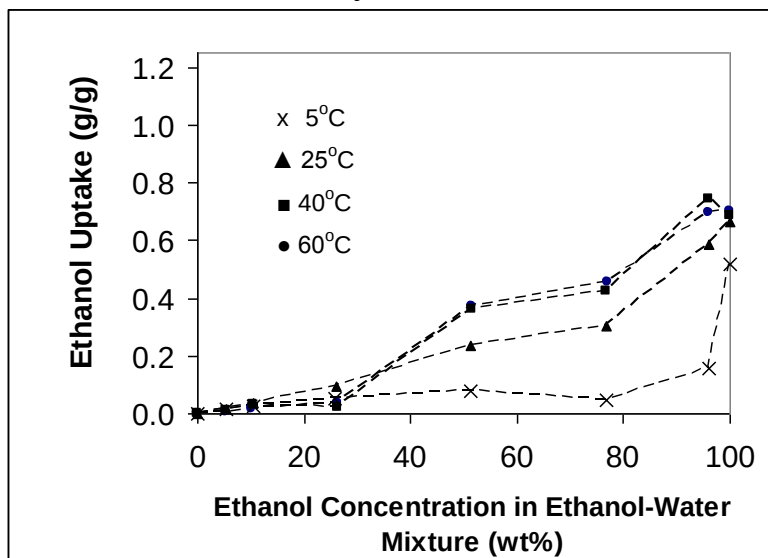


Figure 5. Effect of ethanol concentration on ethanol uptake. Each sample containing 4 g canola meal powder (1.18 mm - 3.35 mm) and 150 g solution was run at room temperature and mixing speed of 130 rpm for 30 min.

4.2.2 Adsorption Mechanism

Canola meal contains approximately 36% crude protein, 3.5% crude fat, 6.1% ash, 12% crude fiber and 33% total dietary fibre on a 10% moisture basis. Carbohydrate content would be 44% (Hassas-Roudsari, et al. 2009; Hickling, 2001). It has been determined that hydroxyl groups on carbohydrates such as cellulose and starch can form hydrogen bond with water molecule (Quintero and Cardona, 2009). Therefore water uptake by canola meal biosorbent may be through hydrogen bonding between water molecules and hydroxyl groups in canola meal. From the results in this study, it was demonstrated that increase of temperature from 25°C to

60°C, decreased the equilibrium uptake. This indicated that the adsorption is exothermic and physical adsorption is predominant. Adsorption through hydrogen bond is a typical physical process. At a low 5°C, water molecule has higher resistance to transport into the inner sites of canola meal, as a result, water uptake is low. In addition, proteins can adsorb water through their polar groups (Kleeberg and Luck, 1984). Contribution of proteins in canola meal for water adsorption needs to be examined in the future work.

4.3. Design of adsorption column system (Phase 3)

4.3.1 Fixed-bed water adsorption system

The fixed bed water adsorption system was established in the laboratory at the University of Saskatchewan in 2009. The system consists of an evaporator to obtain ethanol vapour mixed with water, a stainless steel adsorption column (2.3mm in diameter and 500 mm in height) with water jacket and packed with canola meal biosorbent particles (sieved sizes of 0.25 mm – 1.18 mm), a condenser to cool down the ethanol vapour, and a fraction collector to collect the product. In this process, 10-95 wt% ethanol-water mixture generated from the evaporator enters the adsorption column where water is adsorbed by the adsorbents and ethanol vapour of high purity exits from the column. Finally, the ethanol product is collected through condensation.

Through this process, the biosorbent particles were able to dry ethanol vapour with 90wt% to 4 wt% water content to achieve 99.3 wt% ethanol. The temperature of the dehydration column affected the ethanol dehydration performance, optimized at 85°C. The amounts of biosorbent packed in the column was at 0.54g/L and the average flowrate of the effluent was about 1.5 mL/min. The water saturated biosorbent particles were oven dried at 105°C and re-used. The water uptake of the biosorbent achieved so far in this fixed-bed process was 0.48g/g still higher than molecular sieves (0.20-0.25g/g), and ethanol uptake was 0.068g/g higher than molecular sieves (0.001g/g) (Simo, et al., 2009). As the maximum water uptake of canola meal from the liquid phase was 2.33g/g, the performance of this column system could be further improved.

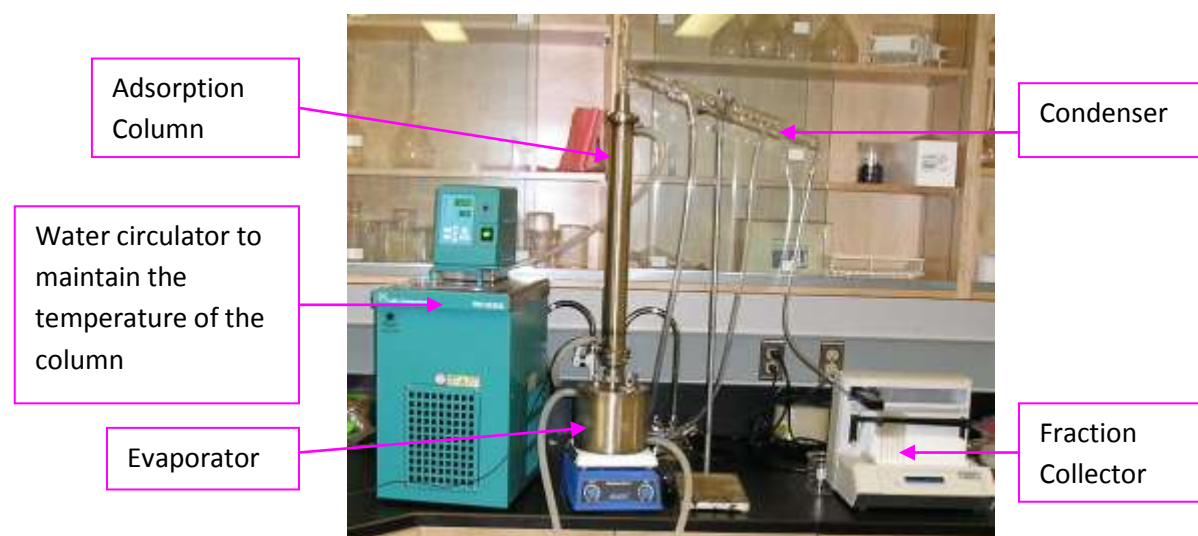


Figure 6. Fixed bed water adsorption system

4.3.2 Pressure Swing Adsorption (PSA) system

PSA system is popularly used in the ethanol industry for ethanol dehydration. The system established in the laboratory at the University of Saskatchewan through this project is composed of a pump, a pre-heater, a column (100mm in diameter and 300mm in height) packed with canola meal pellets and a condenser. 95 wt% or lower grade ethanol-water vapour enters the top of the column under a modest pressure, passes downward through the bed and exits the bottom as ethanol vapour with higher purity. The water saturated canola meal pellets were regenerated online by purging nitrogen under vacuum or by oven dried (preliminary test) at 105°C.

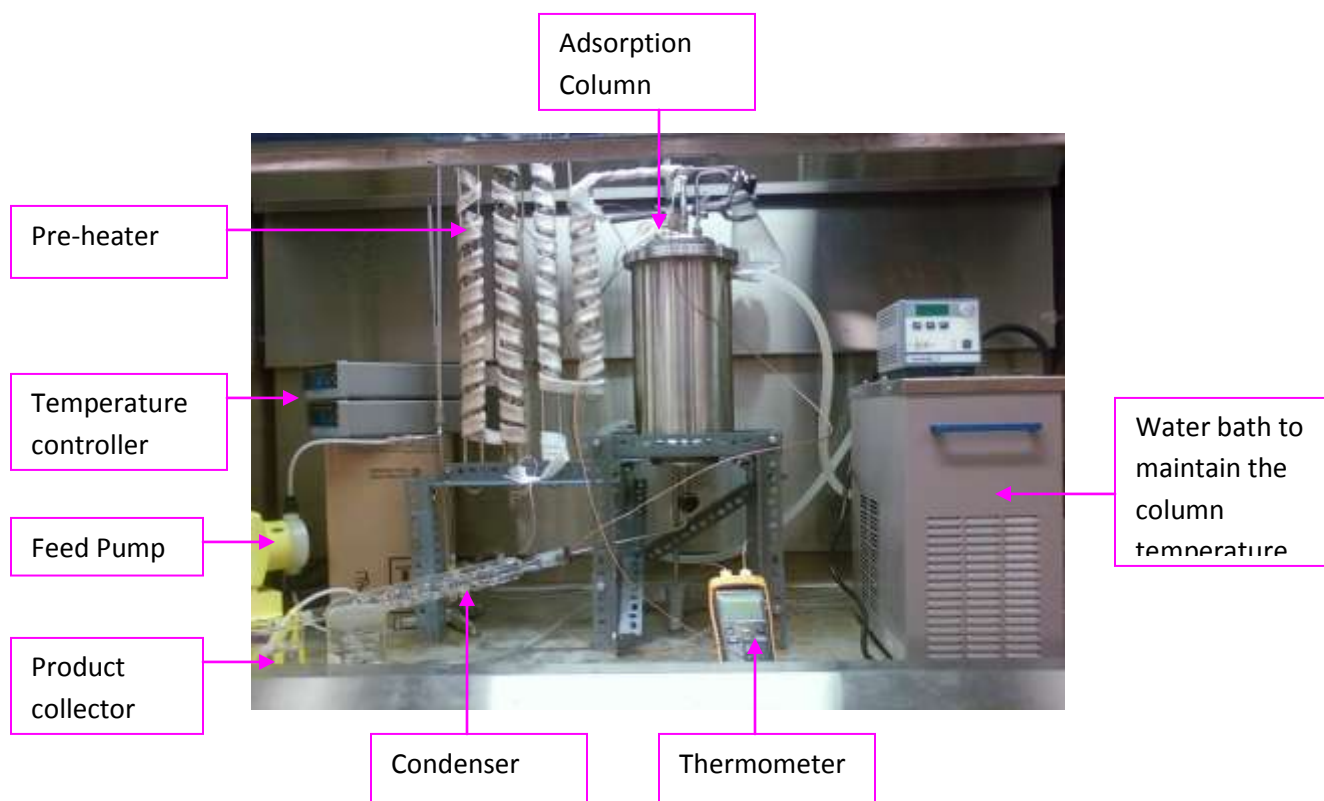


Figure 7. Pressure Swing Adsorption system

The water is adsorbed by the canola meal pellets in the column. The process is shown in Figure 7.

With the canola meal pellets packed in the column, the PSA system is able to dehydrate 95wt%, 80 wt%, and 50 wt% ethanol water mixture to achieve 99.6 wt%, 98.9wt% and 97.5 wt% ethanol, respectively. The temperature and pressure of the column were optimized at 90°C and 25 psi. The temperature of pre-heater was controlled at 160°C and the feed flowrate was at 1 mL/min. The results demonstrated that the canola meal pellets were able to dehydrate ethanol in a wide range of water concentration, which overcomes the limitation of molecular sieves currently used in industrial ethanol dehydration process that can only be applicable to dry 92 wt% - 95 wt% ethanol. This can reduce the energy demand in distillation process.

We further investigated the effects of operation parameters including pressure of 18-22psi, ethanol feed concentration 50-95%, dehydration column temperature 85-105°C and feed flowrate 5-9ml/min. A central composite design was used to determine the interaction of the above mentioned parameters on ethanol dehydration. It has been demonstrated through the central composite design that there is interaction between the column temperature, pressure and feed flowrate and concentration.

The model was generated using Design Expert version 6 using a four factor central composite design

$$C_E = -35.26 + 2.50T + 0.07F + 0.11C_F - 0.59P + 0.03F^2 + 0.19P^2 + 0.017F - 0.04TP + 0.01FC_F - 0.17FP - 0.02C_FP \quad (1)$$

where

T is column temperature (°C)

F is feed flowrate (ml/min)

C_I is initial ethanol concentration (w/w%)

P is final pressure (psi)

C_E is effluent ethanol concentration (w/w%)

C_F is the feed ethanol concentration (w/w%)

It has been demonstrated through the central composite design that there is interaction between the column temperature, pressure and feed flowrate and concentration.

The water saturated canola meal pellets were regenerated online by purging nitrogen under vacuum or by oven dried at 105°C. The pellets enhanced the stability of the canola meal particles. They have been re-used for over a year ago and are still being used without reduced quality.

4.4 Additional results

Upon completion of the above results on canola meal proposed in the original research plan, we have done the following additional results in order to further explore the potential use of canola meal.

4.4.1 Analysis of major composition in the meals

The nutrients including mineral, crude proteins, fats, and moisture contained in fresh canola meal, meals after used for one month, and a year were analysed. Mineral contents were determined by ICP-AES at the Saskatchewan Research Council. Crude protein was analyzed by (AACC Method 46-30). The fat contents in the meals were measured according to AOCS (American Oil Chemist's Society) Ba 2a-38 at the Agriculture and Agri - Food Canada, Saskatoon, SK. Moisture was determined by AOCS Ca 2f-93 where canola meals were dried for 24 hrs in an oven at 105 °C. Ash content was determined using 50 g samples of canola meals by an AOCS method Ba 5-49. The meals were heated in a muffle furnace for 5-6 hours hrs at 550 - 600 °C. Analysis of elements C, H, N, and S was done by an Elemental Analyzer (Vario EL III, Germany). Water and ethanol content in the liquid water and ethanol mixture were determined by a Karl Fisher coulometer (Mettler Toledo DL32) and a Chemical Analyzer (Analox GM8), respectively. A physisorption analyzer (Micromeritics ASAP2020) was used to measure the biosorbent surface area. The results are shown as follows.

Table 1. Contents of major minerals in canola meals (CMs) (dry weight basis)

CMs	Ca (wt%)	Mg (wt%)	P (wt%)	K (wt%)	Ash (wt%)
Raw CM	0.65±0.01**	0.49±0.01	1.05±0.01	0.93±0.02	7.04±0.20
1 month old*	0.79±0.01	0.60±0.01	1.09±0.01	1.11±0.02	7.81±0.20
1 year old*	0.66±0.01	0.62±0.01	1.20±0.01	1.12±0.02	8.20±0.02

*: refer to the time for CM used for ethanol dehydration.

**: standard deviation.

Table 1 shows that the mineral contents of raw canola meal, canola meal used for ethanol dehydration for one month, or one year are quite similar.

The contents of major elements, protein, fat and moisture were also determined and shown in Table 2. The protein content remains similarly for all the three types of canola meals showing the canola meal still has great potential for animal feed after used for ethanol dehydration. In addition, the fat contents are quite similar for the raw canola meal and the one-month used CM. The decreased fat contents of the CM used for one year indicated that part of fat may be removed from CM during ethanol dehydration. However, the amount is still low. Other elements such C, H, S stayed unchanged.

Table 2. Contents of major elements, protein, fats, and moisture of canola meals (CMs)

CMs	N (wt%)	C (wt%)	S (wt%)	H(wt%)	Crude protein (wt%)	Fat (wt%)	Moisture (wt%)
Raw CM	5.75±0.05**	44.10±0.56	0.64±0.02	6.26±0.01	35.71±0.33	4.24±0.22	8.92±0.03
1 month old*	6.50±0.00	48.30±1.34	0.64±0.75	6.90±0.47	40.61±0.06	4.73±0.41	1.06±0.04
1 year old*	6.86±0.14	47.20±1.85	0.83±0.12	6.45±0.26	42.91±0.92	1.66±0.09	1.42±0.01

*: refer to the time for CM used for ethanol dehydration.

**: standard deviation.

The results demonstrated that canola meals after used for ethanol dehydration still retain their major nutrients which have great potential for animal feed.

4.4.2 Water/ethanol adsorption by canola meal after protein extraction

Canola meal becomes important source of protein because of the rich content of protein in it. It is important to investigate whether canola meal after protein extraction has the capability for ethanol dehydration. To that end, canola meal was treated with alkali sodium hydroxide in order to extract protein. The major elements, and protein were analysed by an elemental analyzer (Vario EL III, Germany) and the results are shown in Table 3. In the raw canola meal, protein content is about 44.87wt%. The protein content decreased to 21.87% when treated using 0.3N

NaOH and down to 10.62% using 3N NaOH. Carbon and hydrogen contents remain almost the same. Sulfur content was decreased as well. It demonstrates that alkali treat is effective to extract protein from canola meal.

Table 3. Composition of canola meal (CM) after protein extraction

Adsorbent Type	Nitrogen (%)	Carbon (%)	Sulphur (%)	Hydrogen (%)	Protein (%)
Raw CM	7.18 ± 0.08	47.76 ± 0.02	0.53 ± 0.37	6.78 ± 0.30	44.87 ± 0.53
0.3N NaOH Treated CM	3.50 ± 0.03	46.25 ± 0.84	0.2 ± 0.01	6.98 ± 0.21	21.87 ± 0.06
3N NaOH treated CM	1.7 ± 0.12	45.71 ± 0.51	0.11 ± 0.00	6.83 ± 0.12	10.62 ± 0.92

Canola meal particles treated from the above process was used for water/ethanol uptake test. The results are shown in Table 4. It can be seen that water uptake was increased by canola meal after protein extraction. As the concentration of NaOH increased from zero to 3N, water uptake was increased from 2.34g/g to 9.64g/g, almost 4 times higher, while ethanol uptake was increased only from 0.27 to 0.49g/g, less than two times. The results show canola meal after protein extraction not only has effective and increased water uptake, but also has higher water selectivity over ethanol. It may be because the alkali treatment helps dissociate dense structures of cellulose or hemi-cellulose of canola meal so that more functional sites are available for water uptake. More work needs to be done on investigation of how the protein extraction affects pelletization of such canola meal and its performance for ethanol dehydration. The results show that alkali method is effective to extract protein from canola meal. The canola meal residues after such treatment are still effective for selective water uptake. The research results demonstrated that canola meal either in its raw form or after protein extraction has great potential for ethanol drying in industry. It is worth to further investigate the characteristics of canola meal for this application.

Table 4. Water/ethanol Uptake by canola meal after protein extraction

Conc. Of NaOH	Sample weight (g/g)	Water uptake (g/g)	Ethanol Uptake(g/g)
3N	0.64	9.64	0.49
2.5N	0.64	8.91	0.43
2N	0.64	7.76	0.41
1.5N	0.64	6.57	0.39
1N	0.64	5.64	0.37
0.3N	0.64	5.18	0.35
0 N (Raw CM)	0.64	2.34	0.27

5. Conclusions

The project has been successfully completed on canola meal research according to the original research proposal. We have successfully developed canola meal biosorbents. Two ethanol dehydration column systems, including a regular fixed bed column system, and a Pressure Swing Adsorption (PSA) system, were established in the laboratory at the University of Saskatchewan. The fixed bed system was able to dry ethanol vapour with 90wt% to 4wt% water content to achieve up to or over 99wt% ethanol using the canola meal biosorbents. The column temperature was optimized at 85°C. The Pressure Swing Adsorption (PSA) process which mimics the PSA process in bioethanol plants has successfully used the canola meal cylindrical pellets to dry 50wt% - 95wt% ethanol and obtain 97.9 wt% - 99.6 wt% ethanol. The important parameters affecting the dehydration were investigated including pressure of 18-22psi, ethanol feed concentration 5-95wt%, dehydration column temperature 85-105°C and feed flowrate 5-9ml/min. which effectively concentrated ethanol. The water saturated canola meal pellets were able to be regenerated online by purging nitrogen under vacuum or offline oven dried at 105°C. They have been reused for over a year and have been used without deteriorated quality.

In addition, we investigated that the nutrients originally contained in the canola meal including minerals and proteins did not change significantly in the canola meal pellets after used in ethanol dehydration for over a year. Furthermore, it was demonstrated that water uptake was increased by canola meal after protein extraction using alkali method compared with raw canola meal. The higher the concentration of sodium hydroxide, the higher the water uptake. The results show the great potential of canola meal after protein extraction for ethanol dehydration.

6. Results dissemination

The principle investigator Dr. Catherine Niu was invited to give a talk on ethanol dehydration using biosorbents at the 5th Canadian Ambassador's Science & Technology Roundtable in Berlin, Germany on December 7, 2009.

In July 2010, Dr. Niu gave a talk on introduction of the ethanol dehydration research at the Cambridge of University, UK.

We have presented our results in the following journal or conferences (names of the trained students through this research are in bold):

T. Baylak, P. Kumar, C.H. Niu, and A. Dalai. 2012. Ethanol Dehydration in a Fixed Bed using Canola Meal, *Energy and Fuels*, 26: 5226-5231.

Z. Ranjbar, P. Kumar, A. Dalai and C.H. Niu, 2011. Ethanol Dehydration with Protein Extracted Canola Meal. 61th Canadian Chemical Engineering Conference, London, ON, Canada, October 23-26.

Tajallipour, M., P. Kumar, A. Dalai and C.H. Niu, 2011. Ethanol Dehydration using Canola Meal in a Pressure Swing Adsorption Process. 61th Canadian Chemical Engineering Conference, Ottawa, ON, SK, Canada, October 23-26.

C. Wickens, C.H. Niu and A. Dalai, 2010. Ethanol Dehydration using Biosorbents in a Pressure Swing Adsorption Process. 60th Canadian Chemical Engineering Conference, Saskatoon, SK, Canada.

R. Kaur, P. Chang, A. Dalai, H. Classen and C.H. Niu, 2010. Characterization of Biosorbents Used for Ethanol Dehydration. 60th Canadian Chemical Engineering Conference, Saskatoon, SK, Canada.

R. Kaur, P. Chang, A. Dalai, H. Classen and C.H. Niu, 2011. Characterization of Canola Meal for Ethanol Dehydration Agriculture Bioproducts. Innovation Network Annual Meeting, London, Ontario, Canada.

N. Jaffer, J. Nakoneshny, L. Haeusler, C.H. Niu, A. Dalai, 2010. Removing Water from Ethanol Using Biosorbents. Agriculture Bioproducts Innovation Network Annual Meeting, London, Ontario, Canada.

N. Jaffer, J. Nakoneshny, L. Haeusler, C.H. Niu, A. Dalai, 2010. Dehydration of Ethanol Using Biological Based Adsorbents. Agriculture Bioproducts Innovation Network Annual Meeting, London, Ontario, Canada.

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7. Acknowledgement

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8. Recommendations and further work

Results achieved through this project indicate canola meal has a great potential for industrial application of dehydration of ethanol, other alcohols or gases. To that end, the following facts are important to address:

High water uptake capacity of canola meal biosorbent: The results from the project show that canola meal biosorbent has water uptake from liquid phase up to 2.33 g/g, ten times bigger than molecular sieves (0.18-0.25g/g) (Simo, et. al. 2009; Carmo and Dubulin, 2006). As a result, it can be used to dry ethanol with a wide range of water concentration (5-95 wt%), overcoming the limitation of molecular sieves that can only be applicable to dry 92 wt% - 95 wt% ethanol. This can reduce the energy demand of the distillation process. The pellets were easily regenerated at 105°C lower than that required for regenerating molecular sieves being 220°C-240°C (Simo, et. al. 2009). The pellets have been re-used for over 22 times since they were made about a year ago

and are still being used without deteriorated quality. The high water uptake capacity of canola meal biosorbent could be the key strength for commercialization.

Economic aspects: The best way to commercialize the technology is to directly use the canola meal pellets in the Pressure Swing Adsorption process for ethanol dehydration in bioethanol plant. Then the costs of the canola meal pellets are important. According to the data provided by Canola Council of Canada on Apr 20, 2010, the price of canola meal is \$212.18/tonne. The expenses for pellet making are estimated at \$76/tonne based on the pilot scale test. Then the total costs are about \$300/tonne canola meal pellets. The commercial price of molecular sieves is about \$3/kg, i.e. \$3000/tonne, ten times higher than canola meal pellets. This is a rough estimation. Complete analysis needs to be done based on the production capacity of an ethanol plant, available facility and the final formula of the canola meal biosorbents. This needs to be done through a detailed defined project.

Potential to dehydrate other alcohols or gases: since canola meal has promising capability for ethanol dehydration, it has great potential for dehydrating other alcohols such as methanol, and butanol, and gases such as carbon dioxide, and oxygen.

Challenge of the life time of canola meal biosorbents: Canola meal is natural biomaterial which is degradable. It has been demonstrated that the canola meal pellets have been re-used for one year and are still used without deteriorated quality, however, whether it can last as long as molecular sieves is still in question. Particularly, the performance of canola meal after protein extraction has not been systematically done. How to enhance the stability and durability of the canola meal pellets is a major concern.

Considering the above facts, in order to facilitate the industrial application of canola meal the following work needs to be done.

- Determine the maximum re-usability of the canola meal pellets. Optimization of the pellets of canola meal such as coating with additives, and of operation conditions of the pressure swing adsorption process for ethanol dehydration will be done.
- Investigate the ethanol dehydration by fractions of canola meal, particularly the meal after protein extraction.
- Enhance water selectivity when canola meals are used for drying ethanol.
- Scale-up the pressure swing adsorption process using canola meal based pellets in pilot scale.
- Analyze the economic aspects of using canola meal biosorbents before and/or after protein extraction compared with molecular sieves.
- Investigate the capability of canola meal for dehydration of other alcohols or gases.
- Explore the capability of canola meal for adsorption of heavy metals such as copper, lead, iron and so on in industrial wastewater so as to develop a technology for wastewater treatment.

We have recruited one postdoctoral research fellow, two master of science (M.Sc.) students, and one undergraduate student since September 2010 to continue to carry the research work on ethanol dehydration with canola meal. The residual fund of SCDC will be used to support the above student researchers to complete their work. Dr. Catherine Niu will apply for funding from NSERC to keep canola meal research ongoing and explore other application of canola meal for gases or other alcohols dehydration, and metal adsorption in environment engineering in a hope that application of canola meal in such industries will be fulfilled.

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