

Characterization of Biodiesel Produced from Chicken Fat and Pennycress Oil using Different Concentrations of Basic Catalysts

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Abstract

The production of biodiesel from chicken fat and pennycress oil through esterification and transesterification processes using sulfuric acid (H₂SO₄) as the acid catalyst and different concentrations of potassium hydroxide (KOH) as the basic catalyst was evaluated. This study quantified the effects of the concentration of basic catalyst on the percent of fat conversion and on the yield of biodiesel. The biodiesel was evaluated for its properties as a fuel and compared with the standards of the American Society for Testing and Materials (ASTM) for biodiesel based on its viscosity, flash point, cloud point, and total glycerin by gas chromatography. The results indicated that a concentration of 1.0% KOH at 60°C, with 60 minutes of reaction time and a 6:1 molar ratio of alcohol-oil resulted in the best yield (81.91%) from chicken fat with the highest conversion percentage (96.5%). The yield of biodiesel from pennycress oil was lower (77.44%) than that from chicken fat. The biodiesel obtained under these conditions had characteristics very similar to those described in the ASTM standards for biodiesel.

Keywords: Biodiesel, vegetable oil, animal fat, bioenergy, biofuels

1. Introduction

Biofuels are an important alternative for the current global demand for energy. Biodiesel, bioethanol and biogas have been obtained from a variety of organic materials, such as starch, oilseeds, cellulose and animal fats (Carere *et al.*, 2008). First generation biofuels have shown some limitations related to the resource used in competition with food applications (Montagne *et al.*, 2013). The conflict of using organic materials as either food or the raw material for biofuel production has motivated investigations on the use of non-edible raw materials for producing biodiesel (Guerrero-Fajardo *et al.*, 2010; Montagne *et al.*, 2013). Biodiesel is a renewable and biodegradable fuel and also has higher oxygen content than petroleum diesel. In addition, the use of biodiesel results in a considerable reduction in the emissions of carbon dioxide, carbon monoxide, particulate matter, polyaromatics, sulfur, hydrocarbons, smoke and noise (Demirbas, 2008; Linet *et al.*, 2009; Panneerselvam *et al.*, 2011). The main problem in the biodiesel industry is the availability of inexpensive, abundant, high-quality material. The costs of agricultural input account for between 59% and 91% of the production cost (Kulkarni & Dalai, 2006; Montero *et al.*, 2009).

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This cost is one of the reasons why biodiesel produced from food-grade oils is not yet economically competitive with petroleum-based diesel (Canakci&Van Gerpen, 2011). In response to this problem, the use of less valuable non-edible organic material (Guerrero-Fajardo *et al.*, 2010) or highly acidic waste materials has been gaining increasing importance. The raw material with greater potential for biofuel production in the future will be a number of by-products, wastes, and organisms that have not direct economic benefit for human (Zhang& Zhang, 2012). Producing biodiesel from non-edible oil has great possibilities (Ramning *et al.*, 2013). The pennycress (*Thlaspi arvense*) is a winter annual species; the pennycress seeds typically contain 36 to 40% oil. Pennycress oil exhibits excellent low temperature fluidity which also makes it very attractive for biodiesel production (Olds College Centre for Innovation, OCCI, 2011). The production of biodiesel from these feedstocks regularly requires a catalyzed two-step process. One step is catalyzed by acids, and the other step is catalyzed by bases. The acidity of the materials results from free fatty acids (FFAs) that are converted into soaps in the presence of a base and water. For this reason, this type of raw material cannot be reacted in the classical form (base catalysis) to obtain high yields. The combination of acidic and basic catalysis allows for the use of low-value materials to obtain high yield (Van Gerpen, 2005; Dalla Costa *et al.*, 2006). This study aims to evaluate the production of biodiesel from chicken fat and pennycress oil using different concentrations of a basic catalyst.

2. Materials and Methods

In this study, we used samples of pennycress oil that was provided by the Olds College Centre for Innovation, Alberta, Canada and chicken skin fat obtained from waste slaughter that was provided by a local company in Alberta, Canada. Three replicates for each sample were analyzed to estimate their acid values (AV) according to the American Oil Chemists' Society (AOCS) Ca-5 method (AOCS, 1997). Before the chemical analysis, components other than fat were removed by separation. The initial AV of 9.95 mg/g KOH and 0.62 mg/g KOH were measured for pennycress oil and chicken fat, respectively. The use of acid catalysts has been reported to be successful for the pretreatment of materials with high contents of FFAs to convert the FFAs to esters (Van Gerpen, 2005). The esterification was conducted only in the pennycress oil with an acid catalyst (sulfuric acid) with a 6:1 molar ratio of alcohol-oil at 60°C for 30 minutes with stirring. The sulfuric acid was added at a concentration of 1% relative to the oil to catalyst w/w. Then, the sample was transferred to a separatory funnel and cooled. The resulting layer of methanol-water-acid was located at the top of the reactants. Thus, the resulting layer was extracted by gravitational extraction. The acid value of the extracted sample was remeasured. The transesterification was performed with an alkaline catalyst. Potassium hydroxide (KOH) with concentrations of 0.75%, 1% and 1.25% w/w catalyst-oil and a 6:1 molar ratio of alcohol-oil were used to treat the pennycress oil. This catalyst was added to the mixture resulting from the acid step and was stirred with heating at 60°C for 60 minutes, thus completing a total of 90 minutes between the esterification and transesterification of pennycress oil. For the chicken fat, due to its low acid value, the acid esterification was not performed. The concentrations of basic catalyst were 0.5%, 0.75% and 1% with a 6:1 molar ratio of alcohol-oil and a temperature of 60°C for 90 minutes. The obtained biodiesel was evaluated for its fuel-like properties according to the American Society of Testing and Materials (ASTM) standards. For marketing, pure biodiesel (B100) must meet a set of quality specifications that are in ASTM D-6751. The following table (Table 1) shows the analysis performed and the method used at obtained biodiesel according to the ASTM D-6751 (ASTM, 2002).

Table 1: Test Methods Used in the Analysis of Quality of Obtained Biodiesel

Property	Test Method	Analysis
Flash point	ASTM D93-07	Pensky-Martens Closed
Cloud point	ASTM D2500-05	Cup Tester
Total Glycerin	ASTM D6584-07	Gas Chromatography
Free Glycerin	ASTM D6584-07	Gas Chromatography
Kinematic Viscosity	ASTM D445-06	Viscometry

The data were analyzed using the SAS version 9.0 program (SAS, 2002). An analysis of variance and mean comparison test (HDS) were performed considering a completely randomized design with three replicates for the conversion percentage of pennycress oil and chicken fat into fatty acid methyl ester (FAME) and yield.

Furthermore, the percent yield of methyl esters was calculated using the following equation:

$$\text{Yield}(\text{weight } \%) = \frac{\text{Methylesters}(g)}{\text{oil or fat } (g)} * 100$$

3. Results and Discussion

To obtain biodiesel from oils or fats that contain a significant amount of FFAs, a special process is required. Mittelbach *et al.* (1992) and Liu (1994) and have reported that the oil should not contain more than 1% FFA for basic-catalyzed transesterification reactions, which corresponds to an AV of 2 mg/g KOH. According to Canakci and Van Gerpen (2001) and Demirbas (2008), the acid catalysis must decrease the AV of the mixture to less than 2 mg/g KOH before the basic catalysis can provide satisfactory results. The AV is the most important characteristic of a raw oil in order to determine if it can be trans-esterified directly (Sattanathan, 2015). In this study, the changes in the acid values of pennycress oil samples revealed that the treatment was effective in reducing the AV to optimal levels for the subsequent transesterification step (Table 2). Manufacturing a biofuel is an experimental process that involves tests on experimental conditions like the reaction time required for the process, the reaction temperature, the type of reaction method and the type of catalyst used and its concentration (Ramning *et al.*, 2013). Good biodiesel yields have been reported by authors that employed the two-step acid-basic catalyzed process in the production of biodiesel (Lin *et al.*, 2009; Wang *et al.*, 2006; Awaluddin *et al.*, 2010). The basic catalyst was used in the pennycress oil samples pretreated with 0.75%, 1.0% or 1.25% KOH. For chicken fat, the concentrations of basic catalyst used were 0.5%, 0.75% and 1%. Furthermore, the percent yield of methyl esters was higher with 1% of catalyst, as shown in Figures 1 and 2.

Table 2. Initial and Final acid Values of Pennycress oil Pretreated with a 6:1 Molar Ratio of Alcohol-oil and 1% w/w H₂SO₄ at 60°C for 30 Minutes and Treated with 0.75%, 1.0% or 1.25% KOH

Treatment	AV initial mg KOH/g	AV final mg KOH/g
0.75% KOH	9.94	1.2
1.0% KOH	9.96	1.42
1.25% KOH	9.96	1.64

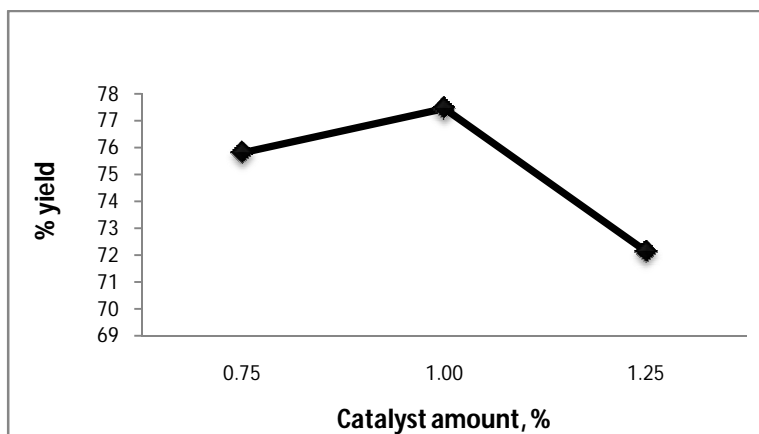


Figure 1. Effect of the Amount of Catalyst on the Yield of Biodiesel from Pennycress oil (60-Minute Reaction time at 60°C with a 6:1 Molar Ratio of Methanol-oil)

When using chicken fat, the biodiesel yield had a tendency to increase as the amount of catalyst was increased. Due to this, the maximum performance will likely be obtained with a catalyst percentage greater than 1.0% (Figure 2). This finding is in contrast with a previous study (Panneerselvam *et al.*, 2011) in which the percentage of catalyst used was minor under similar conditions.

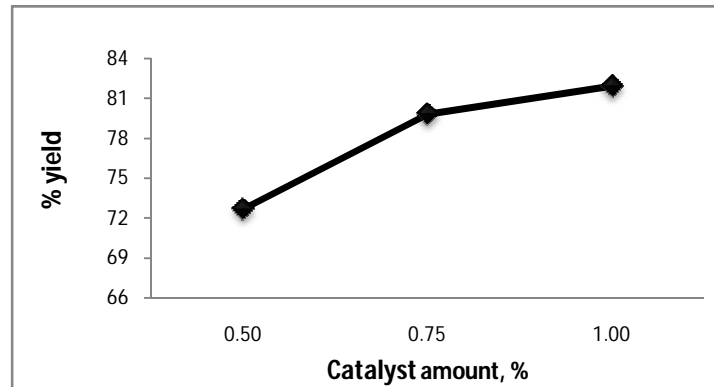


Figure 2. Effect of the Amount of Catalyst on the Yield of Biodiesel from Chicken fat (90-Minute Reaction Time at 60°C with a 6:1 Molar Ratio of Methanol-Oil)

In addition, the conversion of triglycerides (TG) was minor when a low concentration (<1%) of catalyst was used. This conversion increased as the amount of catalyst increased. When 1% KOH was added, 99.7% of TG was converted into FAME. However, in the case of pennycress oil, when the amount of catalyst exceeded 1%, the rate of conversion increased minimally, as shown in Figures 3 and 4.

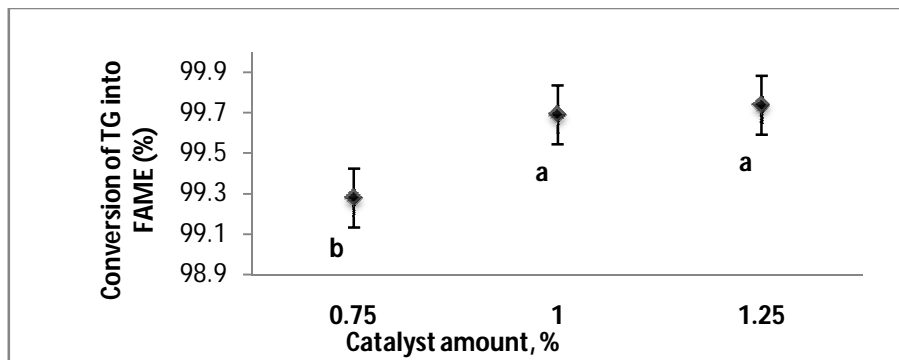


Figure 3: Influence of the amount of catalyst on the percentage of pennycress oil converted into FAME (reaction time of 60 minutes at 60°C with a 6:1 molar ratio of methanol-oil). Different letters indicate significant difference at the P=0.05 level

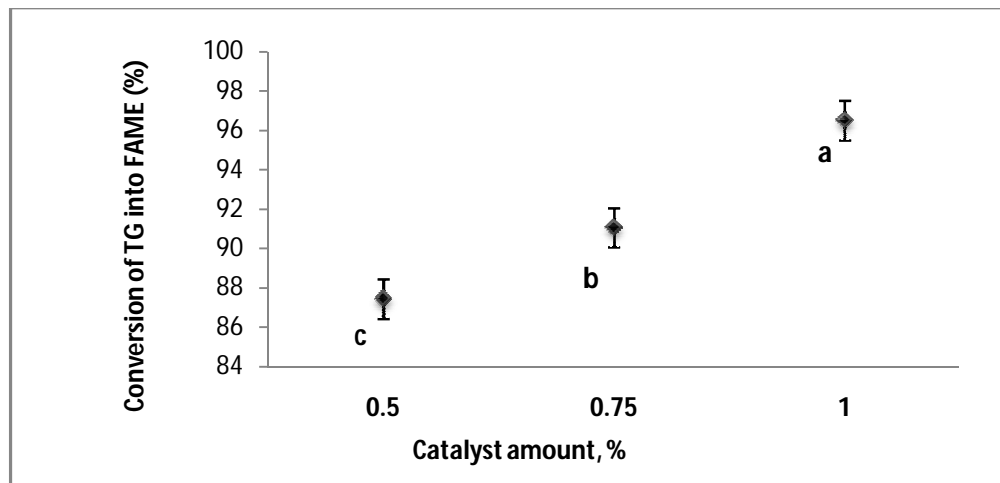


Figure 4: Influence of the amount of catalyst on the percentage of chicken fat converted into FAME (reaction time of 90 minutes at 60°C with a 6:1 molar ratio of methanol-oil). Different letters indicate significant difference at the P=0.05 level

In this work, although the lowest AV was in the chicken fat, the conversion of TG to FAME was minor, which could result from lack of catalyst, because both the conversion as well as the yield, increased when the amount of catalyst was increased, but the maximum performance could not have been achieved with these concentration. This finding reinforces that insufficient amount of catalyst leads to the incomplete conversion of triglycerides into fatty acid esters (Leung & Guo, 2006). The produced biodiesel was evaluated for its fuel-like characteristics based on four major biodiesel fuel properties. The biodiesel was also compared with the ASTM standards. The results are shown in Tables 3 and 4, which indicate that the produced biodiesel met the ASTM standards in the majority of tests. Low viscosity of the oil is the best parameter for performance of the engine. On the contrary, high viscosity causes engine problems such as severe engine deposits, injector chocking, piston ring sticking and difficulty in starting of engine (Knothe & Steidley, 2005). In this study, biodiesel obtained from both pennycress oil and chicken fat showed a viscosity into the range established by ASTM. The lower values of viscosity were found when 1% KOH was used as catalyst.

Table 3: Characteristics of Biodiesel Produced from Chicken fat Compared with the ASTM Standards

Test	ASTM	0.5 KOH	0.75 KOH	1.0 KOH
Flash Point	> 130°C	167.8	175.8	161.7
Cloud Point	---	11	7	6
Viscosity (mm ² s ⁻¹)	1.9-6.0	5.86	5.391	4.92
Total Glycerin(%)	0.24	1.59	1.07	0.44
Free Glycerin (%)	0.02	0.091	0.756	0.361

The cloud point is an important operability parameter. It is used to foresee functionality of engines under cold weather, because it is the temperature where the fuel begins to form crystals (Alleman *et al.*, 2013). The cloud point decreased as KOH increased in pennycress oil and chicken fat. However, the lower values were observed in biodiesel from pennycress (Tables 3 and 4).

Table 4: Characteristics of Biodiesel Produced from Pennycress oil Compared with the ASTM Standards

Test	ASTM	0.75 KOH	1.0 KOH	1.25 KOH
Flash Point (°C)	> 130	147.7	171.7	149.8
Cloud Point	---	-16	-16.75	-17.75
[Viscosity (mm ² s ⁻¹)	1.9-6.0	6.1	5.73	5.75
Total Glycerin (%)	0.24%	0.3	0.24	0.2
Free Glycerin (%)	0.02%	0.010	0.006	0.006

The flash point is defined as the temperature where the vapor above the fuel reaches the lower flammability limit and will ignite under a given set of conditions specified in ASTM D93 (Alleman *et al.*, 2013). The higher the flash point the safer will be to handle and transport. The bigger values of flash point were produced with 0.75% and 1.0% KOH in chicken fat and pennycress oil, respectively.

4. Conclusions

This study of optimizing the process of biodiesel production from chicken fat and pennycress oil showed that the amount of catalyst is one of the factors that affect the production of methyl esters. Based on the results of this study, the following conclusions can be drawn:

1. Pennycress oil and chicken fat may be used as alternative raw materials for the production of biodiesel with good conversion percentages.
2. The amount of FFAs present in the pennycress oil can be reduced to less than 2 mg/g KOH with an esterification process under the following conditions: catalyst of H₂SO₄ acid at 1% w/w catalyst-oil, 6:1 molar ratio of methanol-oil and a reaction time of 30 minutes.
3. The optimal reaction conditions for the production of methyl esters in the case of chicken fat were a 6:1 molar ratio of methanol-oil; 1.0% KOH w/w with respect to the amount of oil, and reaction time of 90 minutes at 60°C. The maximum conversion percentage was 96.50% with a yield of 81.91% under these reaction conditions.
4. The best conditions for the production of biodiesel from pennycress oil with a conversion percentage of 99.69% and a yield of 77.44% were the following: 6:1 molar ratio of methanol-oil; 1.0% KOH w/w relative to the amount of oil, and 60 minutes of reaction at 60°C.
5. The biodiesels obtained from chicken fat and pennycress oil using the process described above have characteristics very similar to those described by the ASTM standards for biodiesel, and they can be used as alternative fuels to petrodiesel.

References

- Alleman, T. L., Fouts, L., & Chupka, G. (2013). Quality parameters and chemical analysis for biodiesel produced in the United States in 2011. National Renewable Energy Laboratory. Technical Report. Golden, CO.
- American Oil Chemists' Society. (1997). Official methods and recommended practices of the American Oil Chemists' Society. 5th ed. Champaign, IL.
- American Society for Testing and Materials (ASTM). (2002). Standard Specification for Biodiesel Fuel (B100) Blend Stock for distillate Fuels, designation D6751-02, ASTM Inter.
- Awaluddin, A., Saryono, A., Prayitno, T., & Amri, A. (2010). Transesterification of waste chicken fats for synthesizing biodiesel by CaO as heterogeneous base catalyst. In: PEA-AIT International Conference on Energy and Sustainable Development: Issues and Strategies, 2-4 June, Chiang Mai, Thailand.
- Canakci, M., & Van Gerpen, J. (2001). Biodiesel production from oils fats with high free fatty acids. American Society of Agricultural and Biological Engineers, 44, 1429-36.
- Carere, C.R., Sparling, R., Cicek, N., & Levin, D.B. (2008). Third generation biofuels via direct cellulose fermentation. International Journal of Molecular Sciences, 9, 1342-60.
- Dalla Costa, B.O., Pisarello, M.L., & Querini, C.A. (2006). Procesos de producción de biodiesel: uso de materias primas alternativas y de alta acidez. Universidad Nacional del Litoral, Facultad de Ingeniería Química, Santa Fe, Argentina.
- Demirbas, A. (2008). Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. Energy Conversion and Management, 49, 125-130.
- Freedman, B., Pryde, E.H., & Mounts, T.L.. Variables affecting the yields of fatty esters from transesterified vegetable oils. Journal of American Oil Chemists' Society, 61, 1638-43.
- Guerrero-Fajardo, C.A., Osorio-Leon, I.D., & Sierra-Vargas, F.E. (2010). Evaluación del efecto de la temperatura en la producción de biodiesel con aceite de higuera. Ingeniería e Investigación, 30, 52-61.
- Knothe, G., & Steidley, K. (2005). Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. Fuel, 84, 1059-1065.
- Kulkarni, M.G., & Dalai, A.K. (2006). Waste cooking oil — an economical source for biodiesel: a review. Industrial & Engineering Chemistry Research, 45, 2901-2913.
- Leung, D.Y.C., & Guo, Y. (2006). Transesterification of neat and used frying oil: optimization for biodiesel production. Fuel Process Technology, 87, 883-890.
- Lin, L., Ying, D., Chaitep, S., & Vittayapadung, S. (2009). Biodiesel production from crude rice bran oil and properties as fuel. Applied Energy, 86, 681-8.
- Liu, K. (1994). Preparation of fatty acid methyl esters for gas-chromatographic analysis of lipids in biological materials. Journal of American Oil Chemists' Society, 71(11), 1179-1187.

- Mittelbach, M., Pokits, B., & Silberholz, A. (1992). Production and fuel properties of fatty acid methyl esters from used frying oil. In *Liquid Fuels from Renewable Resources: Proc. of an Alternative Energy Conference*, 1992:74–78. ASAE, St. Joseph, MI.
- Montagne, X., Porot, P., Aymard, C., Querleu, C., Bouter, A., Lorne, D., Cadoret, J-P., Lombaert-Valot, I., & Petillon, O. (2013). Algogroup: Towards a shared vision of the possible deployment of algae to biofuels. *Oil & Gas Science and Technology – Rev IFP Energy Nouvelles*, 5, 875-898.
- Montero, G., Vázquez, A., Sosa, J., Campbell, H., & Lambert, A. (2009). Biodiesel: una opción para recuperar energía de aceites vegetales residuales y grasas bovinas. In: *II Simposio de ingeniería de Residuos*, 24-25 September, Barranquilla, Colombia.
- OCCI. Background and Sample of Projects (2011). Retrieved from http://www.oldscollge.ca/occi/research/OCCI_Background_and_Sample_of_Projects.pdf
- Panneerselvam, S.I., Parthiban, R., & Miranda, L.R. (2011). Poultry fat—a cheap and viable source for biodiesel production. In: *2nd International Conference on Environmental Science and Technology*, 6, 371-374. Singapore.
- Ramning, A.M., Ganvir, V.N., Akheramka, A., & Bhattacharyulu, Y.C. (2013). Optimization of neem oil methyl ester using response surface methodology (RSM). *International Journal of Advances in Engineering & Technology*, 6(2), 714-723.
- SAS Institute. (2002). *Statistical analysis system*. Cary, NC.
- Sattanathan, R. (2015). Production of biodiesel from castor oil with its performance and emission test. *International Journal of Science and Research*, 4(1), 273-279.
- Van Gerpen, J. (2005). Biodiesel processing and production. *Fuel Process Technology*, 86, 1097-1107.
- Wang, Y., Ou, S., Liu, P., Xue, F., & Tang, S. (2006). Comparison of two different processes to synthesize biodiesel by waste cooking oil. *Journal of Molecular Catalysis A: Chemical*, 252 (1-2), 107-112.
- Zhang, J. & Zhang, W.J. (2012). Controversies, development and trends of biofuel industry in the world. *Environmental Skeptics and Critics*, 1(3), 48-55.