Direct Production of Biodiesel from Lipid-Bearing Materials, Including Canola

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Abstract

In contemporary biodiesel production it is typical to employ a feedstock that is an isolated lipid, such as vegetable oil, animal fat, or waste grease. This necessitates the prior isolation of the lipids from raw material feedstocks, which adds cost and processing technology to biodiesel production. We have demonstrated that incubation of flaked soybeans directly in alkaline methanol achieves high efficiency transesterification, eliminating the need for prior isolation of the lipid (Haas *et al., J. Am. Oil Chem. Soc., 81(1)*:83-89, 2004). The utility of this *'in situ'* transesterification process for the production of simple fatty acid alkyl esters from other feedstocks, in this case canola seeds, is reported here.

Introduction

The simple alkyl esters of fatty acids have numerous uses in the food, textile, cosmetic, rubber, metal processing, and synthetic lubricant industries. Fatty acid methyl esters (FAME) are the predominant esters of fatty acids, with a year 2000 global consumption of 1 million metric tons (1). In addition, FAME are the favored starting material for a variety of derivatives whose annual consumption amounted to 6.2 million metric

tons in 2000 (1). Production and consumption of FAME are rapidly increasing due to their growing new use as biodiesel.

Presently, the majority of FAME are synthesized by alkali-catalyzed transesterification of refined lipid feedstocks, predominantly soybean oil in North America and canola oil in Europe. The oil isolation process contributes to the cost of the finished oil, and ultimately to the cost of the biodiesel product. In addition, the use of hexane in large scale oil extraction results in solvent losses to the environment, an issue of concern to public health regulators, and thus also to oil producers. Therefore, there is interest in reducing or eliminating the use of hexane in oilseed extraction. In addition, probably the largest single impediment to wider adoption of biodiesel is its cost. When produced from refined oils, feedstock cost contributes more than 70% to the cost of the ester product (2). Thus, there is interest in reducing feedstock cost in biodiesel production. A method of biodiesel synthesis that allowed the producer to retain the economic value of the lipid-depleted meal, which is generally sold into the animal feed market, would effectively reduce the feedstock cost for biodiesel production.

Using flaked soybeans as the test material, we recently demonstrated the production of FAME by direct incubation of an oilseed in alkaline alcohol (3). This could eliminate the expense associated with solvent extraction, simplify the process of ester production, and perhaps decrease the cost of biodiesel production. We describe here some features of the reaction. In addition, we present preliminary data showing that the *in situ* transesterification method can be applied to other lipid containing materials, demonstrating its use for FAME production from canola seeds.

Materials and Methods

Chemicals

Flaked soybeans, obtained from a commercial hexane extraction plant, had a thickness of 0.28 to 0.35 mm. Oil content, determined by hexane extraction in a Soxhlet apparatus, was 23.9 wt%. Moisture content, determined by lyophilization, was 7.4 wt%.

Seeds of canola cultivars CN03CL01 (*B. rapa*) and CN03CL05 (*B. napus*) were kindly provided by Drs. J. Daun and D. DeClercq of the Canadian Grain Commission, Winnipeg, CA. The suppliers indicated that the lipid contents of the samples were 46 and 45 wt%, respectively, and moisture levels were 5.5%. Seeds were dried to 0% moisture before use. When desired, the canola was manually ground in a mortar and pestle, or milled to a coarse or a fine flour with an electric mill (Family Grain Flaker and Mill, Cris Enterprises, South Daytona Beach, FL)

Conduct of *in situ* transesterification

The lipid bearing substrate (5.00 g) was mixed with methanol in which sodium hydroxide had been previously dissolved ('alkaline alcohol') in screw-capped bottles of capacity at least 5 times the reaction volume. These were mixed at desired temperatures by orbital shaking at a speed sufficient to keep the solids suspended. Following reaction, the liquid phase was removed and the solids were washed twice by resuspension in 10 mL methanol. Washes were pooled with the main reaction liquid. The tri-, di- and monoacylglycerol (TAG, DAG, MAG), free fatty acid (FFA) and FAME contents of these solutions were quantitated by high performance liquid chromatography (HPLC).

To study the effects of water removal on the reaction, soy flakes were incubated in a convection oven (77 ^{o}C) till desired final moisture levels were attained.

Optimization of transesterification conditions

For flaked soybeans, Central Composite Response Surface design methods (RSM, 4) were employed to coordinately investigate the effects and interactions of the amount of alkaline methanol, its NaOH

concentration, and reaction time on the levels of FAME, FFA, and unreacted acylglycerols (AG) in the liquid phase of the reaction. Best-fit equations correlating the amount of FAME produced with the composition of the reactions were derived using SAS/STAT software (5). Numerical analysis of these equations, and examination of the corresponding 3-D surfaces relating methanol volume and alkali concentration to ester yield, allowed identification of the conditions predicted to give maximum FAME production with minimum contaminating FFA and AG.

Reaction conditions were not optimized for canola.

Results and Discussion

In situ **transesterification of soy flakes**

We have recently shown that it is possible to achieve the direct transesterification of the lipid-linked fatty acids in flaked soybeans soy by simple incubation of the flakes in alkaline methanol (3). The physical appearance of the flakes themselves is changed only marginally during this treatment (Fig. 1).
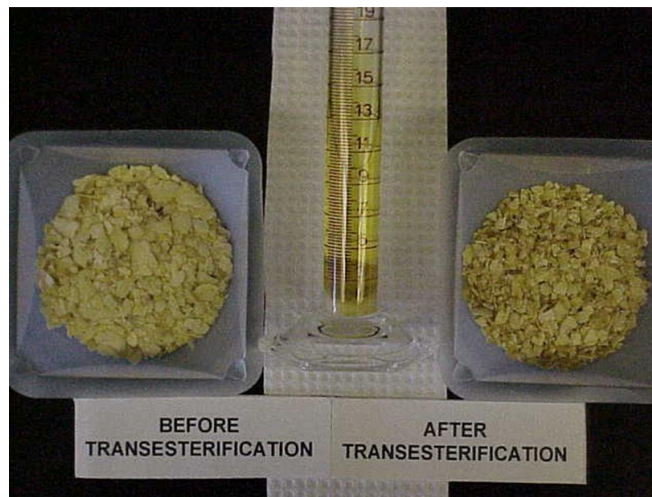
Figure 1. Flaked soybeans before and after *in situ* transesterification, with resulting liquid (alkaline methanol plus fatty acid methyl esters) shown in graduated cylinder.

Optimal conditions for *in situ* transesterification of the soy flakes, as received, determined by RSM, were 30 mL of 0.09M NaOH in methanol per 5 g of flakes, reacted for eight hours at room temperature (3). Of the acylglycerol in the flakes, 95% was converted to FAME. Substantial amounts of acylglycerols and FFA were not present in the liquid phase after reaction. Higher temperatures did not appreciably accelerate the reaction.

These reaction conditions correspond to a molar ratio of triglyceride / methanol / NaOH of 1 / 543 / 2. By comparison, the transesterification of soy oil is typically conducted at a triacylglycerol to methanol ratio of approximately 1:6. Because the removal of this large amount of unreacted methanol from the FAME product would greatly increase process costs for the *in situ* method, a means was sought to reduce the alcohol requirement.

Effect of substrate water content on reagent requirement for transesterification

Raw soybeans contain approximately 9% moisture, and much of this is retained through the flaking process. Water is an inhibitor of fatty acid ester transesterification. To identify any effect of endogenous water content on the reagent needs in transesterification, soybean flakes were dried in a convection oven to either 2.6 or 0% residual moisture and RSM was employed to determine the minimum reagent needs to achieve high levels of transesterification.

Table 1 summarizes the optimized reaction conditions and predicted FAME yields for the transesterification of soy flakes as received (7.4 wt% moisture), and partially (2.6 wt% moisture) or fully dried. The use of fully dry flakes reduced the alcohol requirement by 60% (from 30 to 12 mL per 5 gm of flakes), while increasing FAME yield from 95 to 100% of theoretical. Slightly longer reaction times (10 vs. 8 h) were required to achieve

maximum yield with dry flakes. In all cases, TAG, DAG, MAG and FFA levels in the post-reaction liquid phase were below the limits of detection.

Table 1. *in situ* transesterification: optimum reaction conditions and yields as a function of substrate moisture content (substrate: 5 g soy flakes).

Moisture Content (% mass)	Methanol (mL)	NaOH (N)	Reaction Time (h)	Max. FAME (mg)	Yield FAME (%)
7.4	30	0.09	8	981	95
2.6	18	0.10	16	1096	97
0	12	0.10	10	1125	100

Transesterification of canola

Initial experiments were conducted to examine the feasibility of producing FAME from canola seeds. The seeds were oven dried to remove moisture. Despite the small seed size, transesterification reagents are evidently unable to access the interior of canola seeds and catalyze *in situ* transesterification: no detectable FAME were produced when intact seeds from either of the species under investigation were incubated with alkaline methanol.

Grinding in a mortar and pestle did not facilitate reaction at room temperature: no FAME was detected in such reactions. However, transesterification of manually ground seeds did occur at higher temperatures: at 65 $^{\circ}$C

FAME yields of approximately 35% theoretical maximum were obtained for both canola species examined (Table 2). However, FFA equivalent to approximately 15% of the input lipid fatty acids were also found in the FAME solution. This is undesirable, since FFA are not allowed in biodiesel.

Table 2. Application of the *in situ* transesterification method to canola.

Substrate (5 g)	Treatment	Methanol (mL)	[NaOH] (N)	Reaction Conditions	Ester Yield (% theoret.)
B. rapa	hand ground	10	0.4	65°C, 6 h	36
B. napus	hand ground	10	0.4	65°C, 6 h	36
B. napus	milled to flakes	20	0.2	35°C, 2 h	40
B. napus	milled to flour	20	0.2	35°C, 2 h	61
B. napus	milled to flour	20	0.2	65°C, 2 h	69

These degrees of transesterification were achieved with a relatively high concentration of NaOH (0.4 N). We have observed that such alkali levels can be associated with the production of FFA. With 0.2 N NaOH in methanol, FFA were not produced and 40% theoretical transesterification occurred using flaked canola in 2 h reaction at 35°C (Table 2). Successful transesterification at this lower temperature using flaked seeds suggests that physical access of the liquid reactants to the canola seed lipid is a limiting feature in the reaction. In agreement with this theory, transesterification reached 61% in reactions of finely milled canola flour at 35 °C (Table 2). Raising the reaction temperature to 65°C with the flour further increased FAME yield to nearly 70% (Table 2). The work using milled and ground feedstocks was conducted exclusively with *B. napus*. It seems reasonable that similar results would be obtained with *B. rapa*.

These data indicate that *in situ* transesterification can be conducted using canola as a feedstock. The most effective and efficient conditions for the conduct of the reaction with nearly maximum theoretical ester production remain to be elucidated. However, these preliminary data clearly establish this method as a new and potentially useful technique for direct biodiesel production from canola seeds, one that eliminates the need for an oil extraction facility, and captures the value of the meal for the ester producer.

References

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