

Production of ethyl esters from crude soybean oil: Optimization of reaction yields using a 2³ experimental design and development of a new analytical strategy for reaction control

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Introduction

In Brazil, as in many other countries, the first oil crisis in 1973 led to political initiatives to allocate funds for the development of alternative motor fuels. Initially, this program dealt with various types of raw materials and studied different conversion technologies to produce different liquid fuels from renewable resources (*e.g.*, ethanol). In all of its diversity, this broad national program also included efforts to develop vegetable oils and their derivatives for fuels applications. Indeed, this research area received governmental funding up to 1985, when it was discontinued from a general perception that the cost of making biofuels such as biodiesel from vegetable oils would always be greater than the products derived from the already well established petroleum chemistry and technology.

In recent years, ever since the Middle East crisis initiated a new cycle, the concept of producing biofuels from renewable resources regained international attention. In a direct attempt to contribute to this process, several projects were initiated in our country to evaluate the production of biodiesel from agro-commodities available nationwide, that is, ethanol and vegetable oils. In this work, the production of ethyl esters from crude soybean oil has been optimized and new analytical methods for process control have been designed to facilitate the *in situ* evaluation of reaction yields.

Experimental

The optimization study developed herein was based on an experimental design in which three process parameters were assessed in two levels (2³ experimental design): the ethanol:oil molar ratio used for transesterification (6:1 to 10:1), the concentration of the alkaline catalyst (KOH, 0.2 to 0.6% in relation to the oil mass) and the reaction temperature (40 and 70°C). A further expansion of the experimental design was performed at 40°C, with the ethanol:oil molar ratio ranging from 6:1 to 14:1, whereas the KOH concentration varied from 0.2 to 1%.

The reaction yields were initially monitored by size exclusion chromatography (SEC) and, at the latter stage of the project, by Fourier-transformed infrared spectroscopy (FTIR). This method was successfully used to develop a mathematical model which could easily predict *in situ* reaction yields, thus allowing for a direct monitoring of conversion rates inside the transesterification vessel. Development and validation of the proposed model was carried out by multivariate analysis and the data was treated by principal component analysis and partial least squares regression.

Results and Discussion

The optimal conditions for the one-step transesterification of crude soya oil with ethanol, in which an actual ester yield of 95% was obtained, were: ethanol:oil molar ratio of 12:1, KOH concentration of 0.8% in relation to the oil mass and reaction temperatures of 40°C. These conditions were shown to be adequate for the transesterification of used cooking oil as well, and a first scale up experiment, carried out by a factor of 50 in relation to the bench scale, was also proven perfectly feasible. Lower molar ratios were also proven adequate when reaction times longer than 1 h were used.

Four replicates were carried out at the center point of the experimental design to validate the analytical data generated throughout its execution. The relative standard deviation of the process, including all steps ranging from sampling to SEC analysis, was shown to be only 1.6%. Hence, the overall trends demonstrated by the experimental data were considered of sufficient statistical significance to back-up the proposed conclusions and process recommendations.

In respect to the experimental design, there was a certain limitation in increasing both the ethanol:oil molar ratio and the concentration of the alkaline catalyst (KOH) for further increases in reaction yield. Also, for reactions carried out for more than 20 minutes, temperatures above 40°C were detrimental to the amount of ester produced. In this regard, since the reaction was always carried out in one single step, it seemed that yields could be increased if a two-step transesterification strategy is included, probably using lower ethanol:oil molar ratios.

The FTIR model developed in this work to follow up *in situ* reaction yields was proven very useful and much more effective than traditional methods such as gas-liquid, size exclusion (SEC) and reverse-phase chromatography. The model matched almost perfectly the experimental data obtained by SEC, with a R^2 of 0.984. This is certainly one outstanding achievement because both methods, regardless of differences in their principles, provided almost identical reaction yields for most of the time in which the reaction was followed.

The ethyl esters produced in this work were proven very appropriate for fuels applications. Tests were recently conducted in stationary diesel engines and the results were very promising in both fuel performance and emissions. Longer field tests, similar to those previously done in Curitiba (PR) with methyl esters produced from soybean oil (B20 mixtures), are solely awaiting for a greater local availability of this biofuel, which is now being synthesized in amounts by far below the least requirements for field trials. Therefore, viability of the process is still depending upon a reasonable scale up to a pilot plant level, whereby a suitable cost assessment should indicate how far are we from implementing this process in our country.

Future perspectives

Biodiesel is, by many, one almost irresistible alternative to diesel oil since many environmental as well as socio-economic benefits would readily arise from its utilization in both transportation and energy generation. In Brazil, there has been an increasing interest in developing such an alternative but the economics of producing biodiesel from vegetable oils have always been negative. However, several factors are indicating that changes are just around the corner. These include the severe retraction recently observed in the soybean oil market, the competition of the soybean oil with vegetable oils derived from other sources (e.g., rapeseed, sunflower, palm, dendê and others), the recent decline in exportation of the edible oil to Asian markets such as China, and the several consecutive annual records recently attained in soybean production in Brazil (with the concomitant increase in productivity as well).

To our knowledge, only five Brazilian institutions are now directly involved with biodiesel: The State University of Santa Cruz (Ilhéus, BA), The COPPE School of Engineering (Rio de Janeiro, RJ), The Technology Institute of Paraná (TECPAR, Curitiba, PR), The National Institute of Technology (INT, Rio de Janeiro, RJ) and our institution. Some local representatives of the private sector are also investigating this new business opportunity, such as Risotolândia Indústria e Comércio de Alimentos Ltda. and the State Association of Sugar and Alcool Producers (ALCOPAR, Curitiba, PR), among others. Therefore, there is an increasing perception that biodiesel will soon become competitive and its use in replacement to diesel oil will increase steadily. However, cost barriers among with powerful lobbies are still dominating the area and only a strong political support from all Brazilian soybean producers to these new market opportunities will possibly overcome these barriers. Besides, how could biodiesel be produced if no oil is available to do so? Therefore, the future of biodiesel (and its environmental benefits) in Brazil now resides with the farmers and their sight to the immediate needs of our economy and/or society.