STOCHASTIC MODELING OF BIODIESEL PRODUCTION PROCESS

Sheraz Abbasi, Urmila Diwekar
University of Illinois -Chicago
Chicago, Il 60680

Abstract

There are inherent uncertainties in the biodiesel production process arising out of feedstock compositions, operating parameters and mechanical equipment design and can have significant impact on the product quality and process economics. The uncertainties are quantified in the form of probabilistic distribution function. Stochastic modeling capability is implemented in the ASPEN process simulator to take into consideration these uncertainties and the output is evaluated to determine impact on plant efficiency.

Keywords

Uncertainties, Biodiesel, Feedstock, Stochastic Modeling.

Introduction

Biodiesel is renewable fuel derived from plant oils. It is an alternative to diesel derived from crude oil. Biodiesel burns cleaner than conventional diesel since it does not contain any sulfur content in it. It is derived from various plant and vegetable oils. Refined biodiesel consists mainly of fatty esters, free fatty acids and some triglycerides. Biodiesel feedstock consists of vegetable oils, animal fats and recycled grease. In US, biodiesel comes mainly from Soybean bean oil, tallow and some palm oil. Plant derived oils contain high percentage of triglycerides which are very large molecules. Before these oils can be used in an internal combustion engine, these triglycerides need to be broken down to reduce their viscosity. This process involves transesterification and involves breaking down triglycerides to methyl esters. One mole of triglyceride reacts with three moles of methanol to yield three moles of methyl ester and one mole of glycerol. Biodiesel feedstock is classified according to the content of: 1) triglyceride, 2) free fatty acid. The quality of the biodiesel produced depends on the fatty ester content. The triglycerides found in biodiesel are: 1) Tripalmitin, 2) Triolein, 3) Tristearin, 4) Trilinolein, 5) Trilinolenin. The amount of triglyceride contents varies with the feedstock. The type and amount of triglycerides in the feedstock varies considerably because of nature as a bio-based material.

Background

The biodiesel production process involves feedstock reaction in either plug flow reactor, batch reactor or continuous stir tank reactor (CSTR). The feedstock consists of the oil, typically soybean oil, methanol in a 6:1 molar ratio, and a catalyst (sodium hydroxide or sodium methoxide). The oil feedstock along with methanol and the catalyst is fed to the reactor. The product leaving the reactor is sent to an atmospheric tank where it settles out into two layers: 1) oil plus methanol, 2) glycerol plus methanol. The methanol and glycerol are separated in a distillation column. From the oil plus methanol layer, methanol is removed in a distillation column. The remaining liquid is consists of un-reacted triglycerides which are recycled, free fatty acids and methyl esters. Un-reacted triglycerides are decanted off by washing with hydrochloric acid and the remaining fatty acids and methyl esters which remain form purified biodiesel. This biodiesel is later on blended with gasoline in various ranges as per the requirement of the market.

There are several uncertainties in the biodiesel production process. These uncertainties are due to the nature of the biobased based feedstock. This also directly leads to different processing conditions.

Problem Statement and Approach

The overall objective of this study is to evaluate the impact of uncertainties on the production of biodiesel by evaluating the amount of biodiesel produced (methyl ester plus free fatty acid) and the quality of biodiesel produced (methyl ester content). This evaluation allows a determination of the plant efficiency which could impact process economics.

The uncertainties which are considered in this study were: 1) Uncertainties in the feedstock, 2) amount of methanol produced, 3) reactor operating temperature. The approach taken is as follows: To evaluate the impact of the above mentioned uncertainties, the approach taken is:

- Prepare ASPEN model of biodiesel production process
- Specify a fixed mass input to the reactor.
- Vary the composition of the feed by varying the amount of triglyceride feed to the reactor.
- Vary the methanol flow and operating temperatures

To achieve the above, following procedure adopted was:

- Use of stochastic simulation block in ASPEN
- Uncertainties in feed composition are assigned a probabilistic distribution function.
- Graphical analysis of the output results

Stochastic Modeling

Stochastic modeling approach involves the following procedure:

1. Specifying uncertainty in key parameters
2. Specifying the correlation structure of any independent parameters
3. Sampling the distribution of the specified parameters in an iterative fashion
4. Propagating the effect of uncertainties through the process flow
5. Applying graphical and statistical techniques to analyze the results.

The benefits of this technique are:

1. Uncertain parameters can be described
2. Impact of uncertainties can be evaluated by describing an output variable and drawing the cumulative probability distribution (CFD) graphs

Once probability distributions are assigned to the uncertain parameters, the next step is to perform sampling operations from the multi-variable uncertain parameter domain. In the stochastic modeling used in this study, Hammersly Sequence Sampling (HSS) technique (Diwekar, 2008) is used for efficient evaluations. HSS uses and optimal design scheme for placing the n points on a k-dimensional hypercube. This scheme ensures that the sample set is more respresentative of the population, showing uniformity properties in multi-dimensions, unlike Monte Carlo or other sampling techniques.

ASPEN Biodiesel Model.

For the ASPEN biodiesel model, a CSTR is used as the reactor. Triolein (oleic acid triglyceride) is the triglyceride is only triglyceride which is available in the ASPEN property databank. Other triglycerides are not available in the ASPEN property databank and therefore triolein is used. The oil feed flow to the reactor is kept at a constant 10000 lb/hr. A calculator block is used so that as the triglyceride flow to the reactor increases, a corresponding decrease in free fatty acid flow rate is observed and also vice versa. The flow of triolein to the reactor is represented by a normal distribution curve. The reaction kinetics are considered to be power law and second order with respect to triolein. The value of the pre-exponential factor is assumed to be k=1e5 and activation energy is A=13 kcal/mol. No competing side reactions are considered because physical property data for other triglycerides commonly found the biodiesel feedstock is not available in ASPEN. The range of uncertainties in the biodiesel production that was characterized using literature data is shown in Table 1.

Table 1. Uncertainties in input parameters

Parameter	Distribution	Percentile	
		0.1^{th}	0.9^{th}
Triolein lb/hr	normal	4000	8000
Methanol lb/hr	normal	1200	1700
Reactor temp F	normal	140	200

The probability distribution of the input parameters is shown in figure 1 to 3.

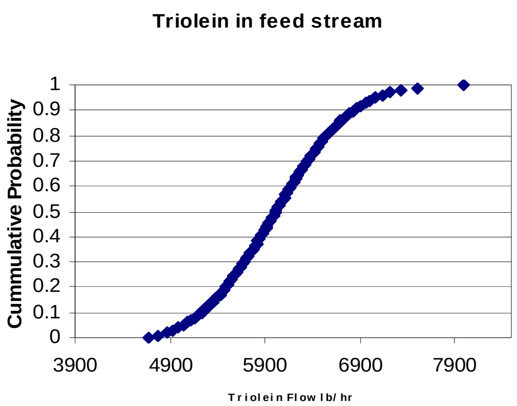

Figure 1. Triolein in feed stream

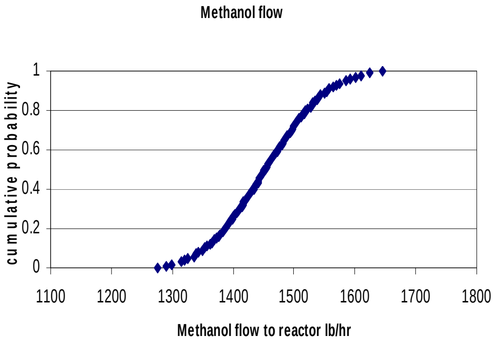

Figure 2. Methanol feed to reactor

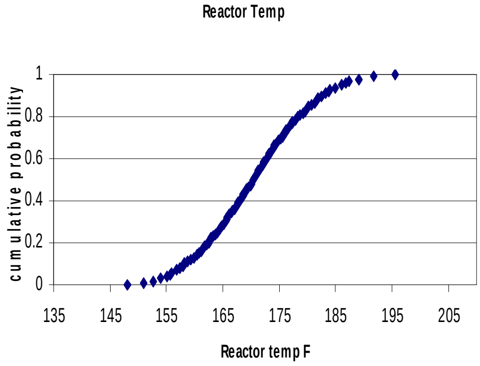

Figure 3. Reactor temperature

Results and Discussion

The results of stochastic modeling are shown in figure 4 to 6. The output variables of stochastic modeling are set as: 1) biodiesel produced lb/hr, 2) methyl oleate (methyl ester), 3) unreated triglyceride.

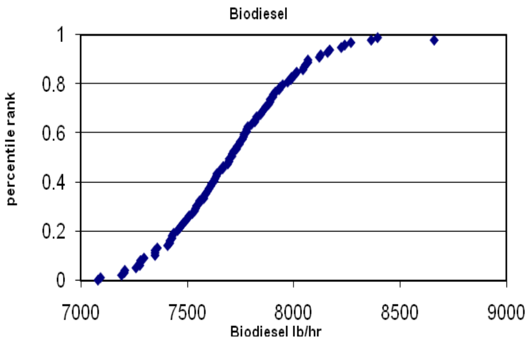

Figure 4. Biodiesel Production lb/hr

Table 2 Biodiesel Production		
Min	Max	Range
7077.844	8658.948	1581.104
MEAN	MEDIAN	VARIANCE
7708.867	7701.329	91162.38

Plant efficiency is determined by considering the methyl ester produced per hour based on the feed flow rate of 10000 lb/hr of oil. The plant efficiency is based on a single pass transesterification and single pass conversion of triolein in the reactor and single pass separation. No recycle of unreacted triglyceride or separated methanol is considered.

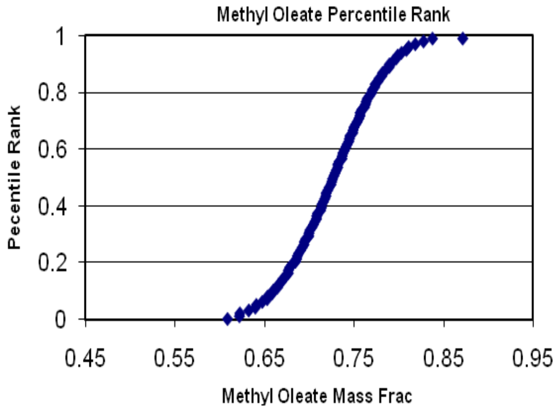

Figure 5. Methly-oleate mass fraction in biodiesel

Table 3 Methlyl Oleat Mass Fraction		
Min	Max	Range
0.6088414	0.8717907	0.2629493
MEAN	MEDIAN	VARIANCE
0.7268474	0.7270023	2.62E-03

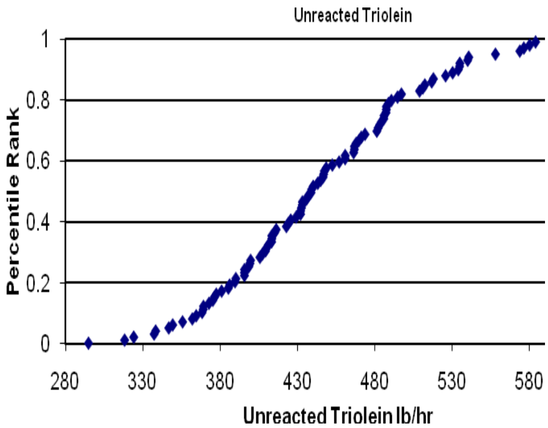

Figure 6. Unreacted triglyceride

Table 4 Unreacted Triolein		
Min	Max	Range
294.6475	593.9769	299.3293
MEAN	MEDIAN	VARIANCE
443.8207	438.8737	4128.745

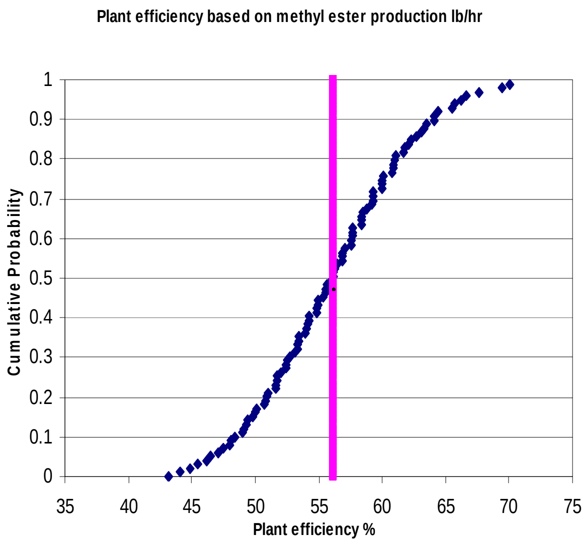

Figure 7. Single pass plant efficiency

The joint contribution of the three input parameters is shown on the plant efficiency. The center line is a base case value with 45% triglyceride in the feed, reactor temperature of 160 F and methanol flow of 1500 lb/hr. The base case plant efficiency is about 56%. By considering a triglyceride content range from 40% to 80%, the plant efficiency also varies from 43% to 70%. The is range of values for plant efficiency demonstrates that:

- Plant efficiency is not linearly related to the triglyceride content of the oil.
- The impact of uncertainties on the production of biodiesel is significant
- The wide range in plant efficiency highlights that uncertainties in the feedstock composition cannot be ignored because they can have a major impact on the process economics.

Conclusion

This study has described a process for the evaluating the uncertainties in the biodiesel production process. These uncertainties arise out of the feedstock and operating conditions. The uncertainties propagate through the flow sheet and their impact on plant efficiency is significant. The evaluation of uncertainties by using stochastic modeling can be extended to other process pathways for determining plant economics. The results of this study could be used for plant design, R&D and selection of feedstock and determining operating envelops.

Acknowledgments

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