Clean Techn Environ Policy (2014) 16:79–94
DOI 10.1007/s10098-013-0596-4

ORIGINAL PAPER

Characterization and stochastic modeling of uncertainties in the biodiesel production

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Received: 26 September 2012 / Accepted: 22 February 2013 / Published online: 7 March 2013

Abstract There are inherent uncertainties in the biodiesel production process arising out of feedstock composition, operating and design parameters and can have significant impact on the product quality and process economics. In this paper, 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 process efficiency and quality of biodiesel.

Keywords Biodiesel · Stochastic modeling · Uncertainties

Introduction

Biodiesel Background

Biodiesel is a renewable alternative to fossil fuel-based diesel for use in diesel engines. Biodiesel is a renewable alternative to diesel fuel because it is derived from bio-based feed stocks such as plant and vegetable oils and recycle grease compared to fossil fuel-based diesel which is derived primarily from the refining of crude oil (Kinast 2003). The common feedstock for biodiesel manufacturing are (i) plant oils such as soybean oil, cottonseed oil, and canola oil, (ii) recycled greases or oils such as yellow grease, and (iii) animal fat such as beet tallow, pork, and lard (Kinast 2003; Gerpen et al. 2009).

Biodiesel burns much cleaner than conventional diesel because it does not contain any sulfur content. Lifecycle analysis shows that biodiesel contains 2.5–3.5 units of energy for every unit of fossil energy input in its production (Sheehan 1998). Some fossil fuel is consumed in the production of biodiesel in the form of fuel used for farm equipment, transportation (trucks, locomotives), and feedstock for fertilizer, pesticide, steam electricity, and methanol used in the manufacturing process. Biodiesel displaces petroleum at nearly a 1- to 1 ratio on a life cycle basis. Because biodiesel is an energy efficient fuel, it reduces the demand for petroleum based products (Sheehan et al. 1998; Hill et al. 2006; Huo et al. 2008). Biodiesel use as fuel significantly reduces greenhouse gas emissions (GHG). For biodiesel produced from crops harvested from fields which are already in production, GHG including carbon dioxide (CO_2) and NO_x emissions are reduced by 41 % (Sheehan et al. 1998). As an in any other combustion process, the burning of biodiesel releases CO_2 to the atmosphere. However, since biodiesel is derived from plant sources which trap CO_2 during photosynthesis, biodiesel consumption does not add CO_2 to the atmosphere compared to fossil fuel based diesel fuel. Particulate matter and hydrocarbon emissions and diesel fuel combustion are toxic and carcinogenic having an adverse impact on human health. However, using B100 (pure biodiesel) fuel eliminates upto 90 % of these air toxins and B20 (20 % biodiesel blend) reduces air toxins by 20–40 % (Gerpen et al. 2009).

Biodiesel improves the operation of engines even if used in very low concentrations of 1 % by improving the

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lubricity of fuels which helps diesel engines by preventing moving parts from wearing out prematurely. Biodiesel also raises the cetane number of fuels. Compared to other bio-based fuels such as ethanol, biodiesel is easy to use because it can be stored and handled by the same equipment which handles diesel. No additional equipment or no modification is required for its use as a motor fuel and users can expect a completely trouble-free B20 experience (Gerpen et al. 2009). Biodiesel contains 8 % less energy per gallon than typical No. 2 diesel in United States and 12.5 % less energy per pound. Biodiesel similar to fossil diesel does suffer from freezing and gelling in very cold weather (Kinast 2003; Gerpen et al. 2009).

ASTM D6751 definition of biodiesel states that biodiesel is composed of mono-alkyl esters of long chain fatty acids derived from plant oils or animal fats and contains only one ester linkage in each molecule (Gerpen et al. 2009). Biodiesel can be made from methyl, ethyl, isopropyl, and other alcohols, but most literature and commercially available biodiesel consists of methyl esters. Biodiesel specifications are defined by ASTM PS121-99. Plant oils and animal fats contain fatty acids and triglycerides (Kinast 2003; Gerpen et al. 2009). However, composition of these triglycerides vary considerably from feed to feed. Further, there are significant uncertainties in operating parameters for the process of biodiesel production.

Scope of this work

The major sources of uncertainties in the biodiesel production process are (i) the composition of the feedstock in terms of different triglycerides, (ii) the mole ratio of methanol to oil, and (iii) the reactor operating parameters. However, we have found not a single paper addressing uncertainties in bio-based fuel production. This was the key driver behind this paper on stochastic modeling of the biodiesel production process as it allows the capture of the uncertainties in the production process and an evaluation of the impact of those uncertainties on the overall process.

This study takes a flowsheet developed for the continuous transesterification of biodiesel production and uses stochastic modeling to evaluate how the uncertainties affect the flowsheet and impacts the (i) quantity and quality of biodiesel produced, (ii) the physical properties of the biodiesel produced, and (iii) comparison between the output of biodiesel quantity, quality, and physical properties between the deterministic and stochastic models.

Benefits of results of this study

The major benefit of this study is that it allows the capture of uncertainties in the biodiesel production process. By having knowledge of the type of quality, quantity, and physical properties of the biodiesel produced form the various feedstocks the following benefits can be gained.

1. Plant designer can design a more economically efficient plant.
2. Production planners and purchasing can select feedstocks as they have a better knowledge of what feedstock will give what quality and quantity of product.
3. Marketing and sales can get a better handle on profitability of product produced as they know what feedstock will give what quality and quantity of product.
4. Plant operations can get a better understanding of the operation of their plant.
5. A more flexible plant which can handle multiple sources of feedstock could be design.

Biodiesel production technologies

The primary raw materials for biodiesel production are vegetable oils, animal fats, and recycled grease. These feedstocks contain triglycerides and free fatty acids. The secondary feedstock for biodiesel is methanol. Other alcohols are also suitable but methanol is the most widely used and widely researched alcohol used in biodiesel production. Triglycerides react with methanol to form methyl esters. One mole of triglyceride reacts with 3 mol of methanol to form 3 mol of methyl esters and 1 mol glycerol. The reaction is could be either acid or base catalyzed. The reaction is a multistep process with the intermediate formation of diglycerides and monoglycerides. Each step of the reaction is a reversible equilibrium step. The common catalyst which is used commercially is sodium hydroxide, potassium hydroxide, and sodium methoxide. Acid catalysts are considered to be too slow for industrial processing. Acid catalysts are used when the feedstock has high fatty acid content (Gerpen et al. 2004).

The biodiesel manufacturing process is a multistep process involving (i) pre-treatment of the feed, (ii) transesterification of triglycerides in the feed to form methyl esters, (iii) separation process to separate biodiesel (methyl esters), glycerol, and methanol. The pretreatment of feedstock includes a degumming step to remove phospholipids and fatty acids are removed in the refining step. The selection of the type of oil affects the production technology which is selected (Gerpen et al. 2004).

The available process technologies for biodiesel production are

1. *Batch processing* this process include the a stirred tank reactor for transesterification, settling tank for separating the glycerol and methyl esters, batch distillation to remove the alcohol, wash water to remove residual methanol, and then separation of water (Gerpen 2004).

2. *Continuous processing* this version of the process includes a continuous stirred tank reactor CSTR (or series of CSTR for greater extent of reaction). The CSTR design does not insure sufficient mixing and consequently the glycerol product is dispersed in the ester phase driving the reaction backward and reducing the overall product yield. A plug flow reactor (PFR) can also be used in the place of CSTR or a combination of the two. Continuous distillation trains are used for separation.
3. *Acid-catalyzed direct esterification process* if the feedstock has a high content of free fatty acids, adding alkali or caustic will cause saponification. Acid could be used as a catalyst for high free fatty acid feedstocks. After the reaction stop, base is used to neutralize the acid and the product mix is the dried.
4. *Non-catalyzed systems Biox process* cosolvents are designed to overcome the slow reaction time caused by the extremely low solubility of alcohol in the triglyceride phase. The Biox process uses a co-solvent, tetrahydrofuran THF to solubilize the methanol resulting in a faster reaction. After the reaction, the co-solvent is recovered. This system requires a low operating temperature. The co-solvents are usually Environmental Protection Agency (EPA) classified toxic pollutants so environmental impact is a significant concern. The co-solvent must be completely removed from both the glycerol and biodiesel (Gerpen et al. 2004).
5. *Supercritical process* supercritical methanol, ethanol, propanol, and butanol are the alcohols used. This process has high product yields due to the simultaneous transesterification and methyl esterifcation of fatty acids. The reaction time is also reduced. However, the downside of the process is that it requires comparatively higher operating temperatures (250 compared to 60 °C) and very high operating pressures (10–25 MPa). In addition, water is produced as a product. The high equipment, energy, and waste disposal costs make this process unattractive. This process competes with batch and continuous biodiesel production process (Demirbas 2006).

Out of the various processes described, the commonly employed industrial processes are the batch and continuous processes. They are usually preferred over other processes because of their relative simplicity. The complexity of other processes and the volatility of the biodiesel markets make the other processes unattractive (Gerpen et al. 2004).

Biodiesel feedstocks

The feedstock commonly used for biodiesel production are soybean oil, corn oil, rapeseed, lard, tallow, linseed oil, and yellow grease (M311K 2008). Biodiesel feedstock is classified according to the content of triglyceride and free fatty acid. The quality of the biodiesel produced depends on the fatty ester content. The triglycerides found in biodiesel are

1. Tripalmitin based on palmitic acid R = $-(CH_2)_{14}-CH_3$ 16 carbons, (including the one that R is attached to.) (16:0).
2. Triolein, based on oleic acid, oleic: R = $-(CH_2)_7CH = CH(CH_2)_7CH_3$ 18 carbons, 1 double bond (18:1).
3. Tristearin based on stearic acid, stearic: R = $-(CH_2)_{16}-CH_3$ 18 carbons, 0 double bonds (18:0).
4. Trilinolein based on linoleic acid, linoleic: R = $-(CH_2)_7CH = CH-CH_2-CH = CH(CH_2)_4CH_3$ 18 carbons, 2 double bonds (18:2).
5. Trilinolenin based on linoleinic acid, linolenic: R = $-(CH_2)_7CH = CH-CH_2-CH = CH-CH_2-CH = CH-CH_2-CH_3$.

The type and amount of triglycerides in the feedstock varies considerably because of nature as a bio-based material. The other major raw material for biodiesel production is methanol. The choice of catalyst is typically sodium hydroxide or sodium methoxide (Gerpen et al. 2004).

Design and optimization of biodiesel production

The common design variables in biodiesel production are (1) process technology, (2) feedstocks, and (3) operating conditions. The choice of process technology is not a major factor because industrial processes favor either batch or continuous transesterification for a variety of factors (Kinast 2003; Gerpen et al. 2004). The major other factors which influence process design are feedstock availability and the operating conditions. Because of the bio-based feedstock, the percentage of triglycerides and the type of triglyceride in the biodiesel feed varies considerably (18 carbons, 3 double bonds [18:3]).

The following table illustrates the various types of triglycerides and their percentage mass fraction in the different oils used for biodiesel production.

The biodiesel production process is relatively new and the feedstock composition is highly variable, the mole ratio of the oil to methanol and the operating temperature of the reactor also vary considerably. It is difficult to settle on a single stoichiometric ratio of feedstock to methanol because the feedstock components vary considerably. Even in the same feedstock, the range of a single component mass fraction could be very broad. The methanol to oil ratio ranges for 4:1–6:1. The reactor operating temperature also varies considerably as the operating temperature has to be adjusted in situ to improve conversion. For equipment

and plant design basis, the operating temperature typically falls in the 333–367 K range.

Most recently, El-Halwagi et al. considered various soy biodiesel production pathways for optimization (Myint and El-Halwagi 2008). Their team simulated various scenarios and modeled the soy bean oil-based biodiesel using ASPEN. They carried out sensitivity analysis and found that the cost of soybean oil is the largest contributor to the production cost. However, the actual components of the feedstocks create significant uncertainties and are very important in the economic analysis of the biodiesel production process.

Process description

Out of the various biodiesel production technologies, batch and continuous biodiesel production technologies utilizing either a CSTR or PFR or a combination of both are the most commonly used for commercial purposes (Kinast 2003; Gerpen et al. 2004). Continuous biodiesel production utilizing a CSTR was modeled in this study. Figure 1 is a block flow diagram of the biodiesel production process utilized in this study.

The biodiesel production process involves (i) reaction for transesterification and (ii) separation step to separate glycerol, methanol, catalyst, and water.

The reaction step involves transesterification. Figure 2 shows the simplified form of the transesterification reaction and Fig. 3 shows the intermediate steps in the transesterification reaction.

In recent literature, the optimization of biodiesel process pathways has utilized a PFR, and assumed a constant biodiesel conversion of 95 % on the basis of constant feedstock components or assumed a single feedstock component (Myint and El-Halwagi 2008; Ataya et al. 2008a, b). PFR studies have shown that the rate of reaction and conversion of packed bed liquid phase reaction (heterogenous phase) and simple liquid–liquid phase reaction (homogenous phase) reaction is similar (Ataya et al. 2008b). In addition, most recent literature has focused on using the feedstock components to optimize the separation process of biodiesel production (Myint and El-Halwagi 2008; Olivera et al. 2010). This study focused on using a CSTR model in the biodiesel flow sheet because

1. CSTR is easy to model compared to homogenous or heterogenous PFR models. A more detailed discussion is included in the later section of this paper.
2. CSTRs most closely mimic batch reactors in industry.
3. Different triglyceride components in the feedstock can be more easily modeled.
4. Both kinetic and equilibrium reaction information can be utilized.

High temperatures and pressures can transesterify the fats without prior removal or treatment of fatty acids, near atmospheric pressures and longer reaction times are preferred because of the associated equipment and operating costs (Myint and El-Halwagi 2008). A continuous process design is selected due to better performance as result of heat economization, improving product purity and lower capital costs.

The reactor temperature is kept between 140 and 200 °F and the reactor is operated at slight pressures to keep the methanol in the liquid phase. Sodium hydroxide was the catalyst used in this reaction. The molar ratio of methanol to oil was varied between 6:1 and 4:1 with a 4:1 being used as the deterministic case. The reactor is designed for a flow rate of 20,000 lb/h.

Only the triglyceride triolein is available in the ASPEN Plus databank. The remaining four triglycerides which are

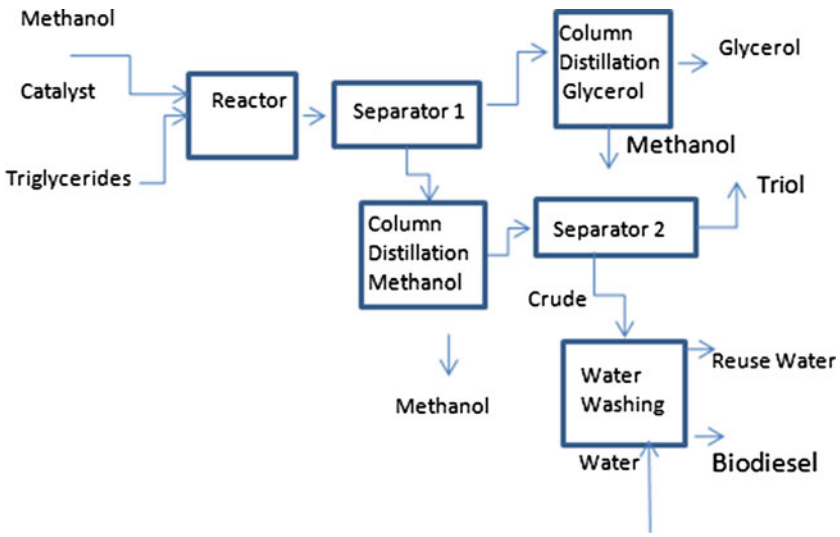

Fig. 1 Block diagram of biodiesel production

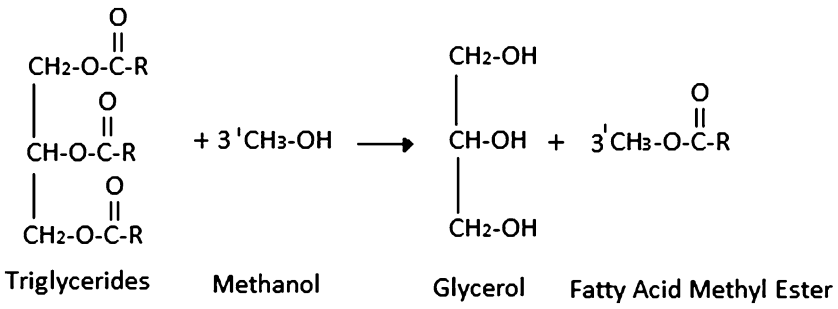

Fig. 2 Simplified form of transesterification (Kinast 2003)

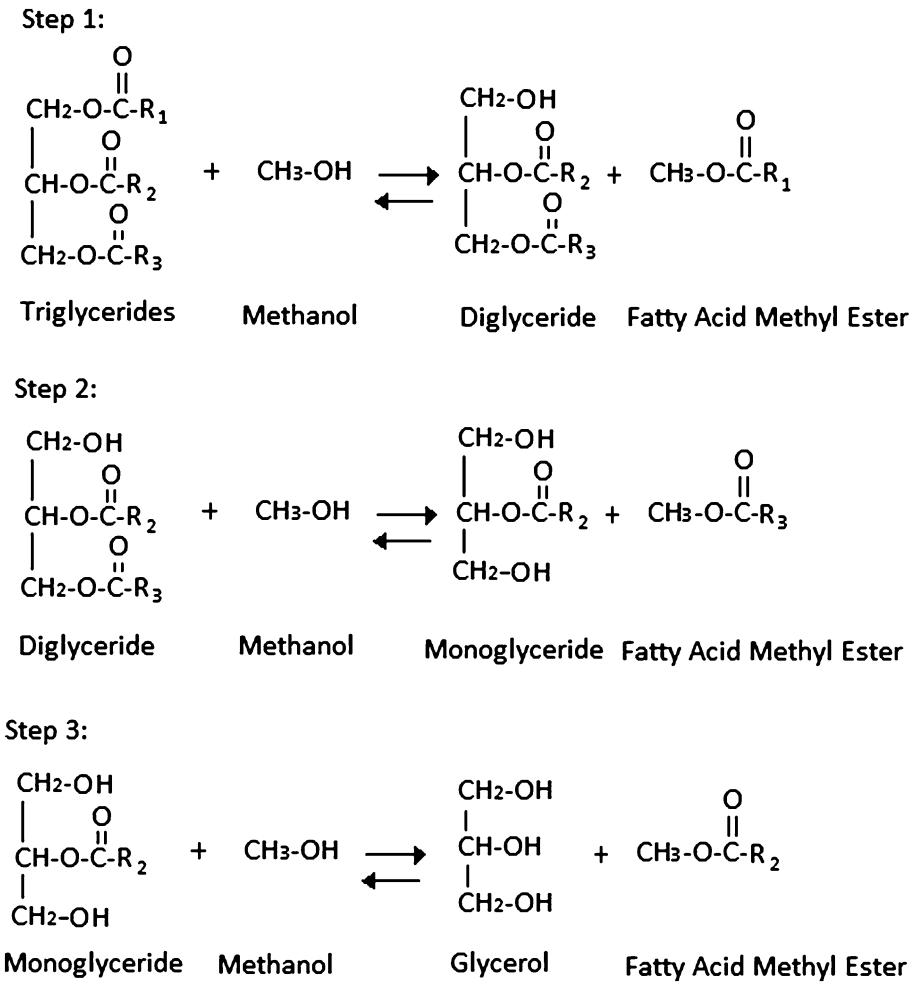

Fig. 3 Intermediate steps in transesterification (Leevijit et al. 2008)

commonly found in the biodiesel feedstocks were added to the ASPEN Plus databank using .mol files and the properties were predicted. RK-Soave thermodynamic equation of state was used to estimate the properties of chemicals in the ASPEN Plus flow sheet. This methodology was a semi-empirical method and is usually used for predicting the activities of non ideal, non-electrolytic systems.

The separation steps include the separation of glycerol, water, and methanol from the reactor product stream. Four different configuration schemes are available (Myint and El-Halwagi 2008):

1. Removal of methanol first: water washing in the presence of glycerol.

2. Removal of methanol first: water washing after removal of glycerol.
3. Biodiesel and glycerol separation first: water washing in the presence of methanol.
4. Biodiesel and glycerol separation first: water washing after removal of methanol.

El-Halwagi et al. have studied the four different configurations and have concluded that scheme 4 is an inherently superior design because (i) less heat duty is required since there is no water and (ii) methanol is recycled back to reactor (Myint and El-Halwagi 2008). The remaining alternatives have inherent operational, contamination, safety and capital, and operation cost-related drawbacks (Myint and El-Halwagi 2008). For example, water wash before methanol removal will cause water to be present in the removed methanol stream and a separation step may be required if the methanol is to be recycled. Scheme 4 was used in this study.

The product leaving the reactor is sent to an atmospheric tank where it settles out into two layers: (1) oil plus methanol and (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 consists of unreacted triglycerides which are recycled, free fatty acids, and methyl esters. Unreacted 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. Commercial biodiesel grades are classified by the blend percentage. The commercially common biodiesel blend is B20.

Problem statement

The overall objective of this study is to evaluate the impact of uncertainties in the production of biodiesel. The specific objectives of the study are

1. Development of base case design of biodiesel production from available literature.
2. Modification of simulation model for stochastic modeling to allow propagation of uncertainties through the flow sheet.
3. Identification and characterization of uncertainties in the biodiesel production process.
4. Evaluation of the impact of uncertainties on the overall production process by considering:

i. Process yields and biodiesel produced,
ii. Physical properties of biodiesel.

To achieve the aforementioned objectives, the following activities were undertaken:

1. Setup of base case biodiesel production flowsheet in ASPEN. This flowsheet included the transesterification reaction section and separation sections. Pretreatment of feed was not considered.
2. The uncertainties in the biodiesel production process included
   i. Feedstock uncertainties—this included the variability in the five triglycerides which are commonly found in most feedstocks.
   ii. Uncertainties in methanol to oil ratio
   iii. Reactor operating temperature uncertainty
3. Characterization of uncertainties and expressing them in the form of probability distribution functions. The distributions define the rule for describing the probability measures associated with the values of a random (uncertain) variable.
4. Development of stochastic biodiesel production model in ASPEN, specifying uncertainties in the stochastic model and specifying the relevant output parameters for study.
5. Simulation of the stochastic biodiesel production model.
6. The evaluated simulation output results which were
   i. Mass fractions of the methyl esters corresponding to the triglycerides in the feedstock steam.
   ii. Single pass process efficiency based on methyl esters in the product stream.
   iii. Physical properties of the biodiesel: specific gravity, specific heat, viscosity, and boiling point of biodiesel,
7. Comparison of outputs with deterministic model. The physical properties of biodiesel produced were also compared with those of fossil diesel.

Figure 4 is a schematic of the approach taken

Characterization of uncertainties and stochastic modeling

ASPEN biodiesel model

The ASPEN databanks has only one component triglyceride: triolein. The remaining four triglycerides: tripalmitin, tristearin, trilinolein, and trilenolenin, are not available in the ASPEN data bank. ASPEN does have the capability for custom components by either drawing the structural formula of the chemical components or importing their structural formula in the form a .mol file and the estimating the physical properties and vapor liquid equilibrium (VLE) data of the components. .mol files for the four triglycerides are available on the internet (http://www.chemicalbook.com/). The .mol

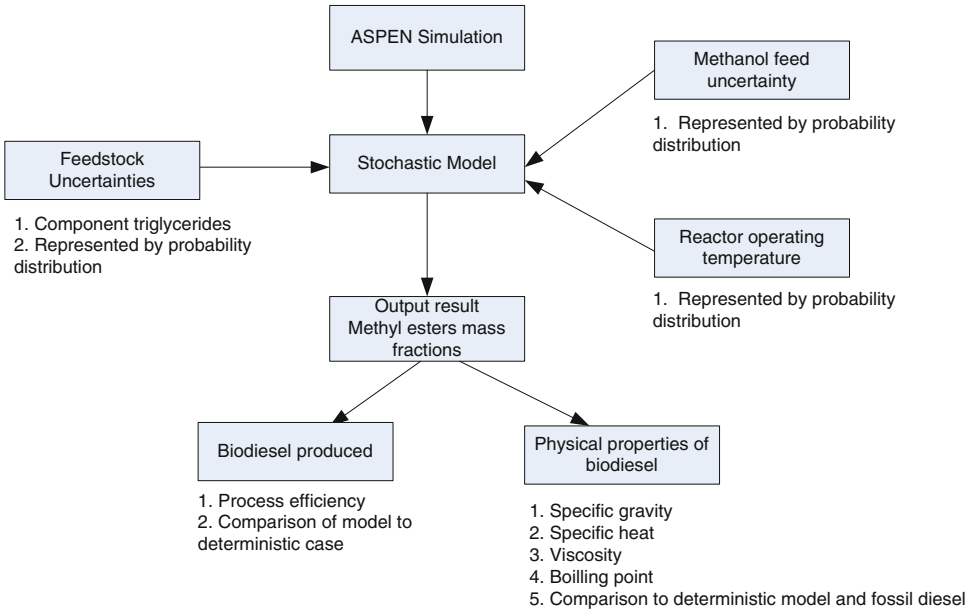

Fig. 4 Schematic of stochastic modeling approach

files for the four triglycerides were imported in ASPEN and the physical and VLE properties estimated from them. RK-Soave was the property method used for the simulation.

As stated earlier, the raw material feed to the reactor is mixture of five triglycerides (triolein, tripalmitin, tristearin, trilinolein, and trilenolenin); a fraction of the feed consists of free fatty acids (FFA) and water. Pure streams of triglycerides and a single stream of FFA and water enter a mixer block. Design specification is used in ASPEN to maintain a constant feed flow rate of 15,000 lb/h into the reactor. This is accomplished using a design specification block, the reactor feed being the specified variable and water plus FFA as the manipulated variable. Methanol was the other feed stream to the reactor. Sodium hydroxide in aqueous form was the catalyst.

The transesterification reaction section includes a CSTR. PFR and combinations of CSTR and PFRs have been used to model the biodiesel production processes. However, these models have used either a single triglyceride (triolein which is available in ASPEN) or assumed a constant conversion rates. This study is using five triglycerides as active components in the biodiesel feedstock, but the component properties of only one triglyceride are available in ASPEN databank. A PFR model requires correlation coefficient for heat and mass transfer which are not available for all components, and hence the reactor model becomes unsuitable. In addition, PFR models for multiple reactions require rigorous reactor sizing with relatively limited benefits to the overall objective of this study. CSTR is both simple to size and model and is widely used commercially in biodiesel production and was therefore used in this study.

Transesterification reactions are reversible reactions with intermediate di- and triglyceride. .mol files for the di- and triglyceride intermediates are not available on the internet nor are the components available in ASPEN data banks. Kinetics of transesterification have been studied by Nourredini et al. and Freedman et al. (Noureddini and Zhu 1997; Dunn 2002; Dufek et al. 1972, 1978; Freedman et al. 1984). Kinetics of overall conversion was estimated from overall conversion. All reactions were considered to be power law, second order based on the triglyceride. The reactor volume was oversized to increase the feed residence time allowing the reaction to go to near equilibrium conversion so that the effects of the reversible reaction can be ignored.

El-Halwagi et al. recently looked at the optimization of the biodiesel production process (Myint and El-Halwagi 2008). They considered four different separation pathways and adopted the separation scheme of glycerol separation first, followed by methanol separation, wash water addition, and decant of wash water. This same separation scheme was used in this separation flow scheme.

Stochastic modeling block was inserted in the flow sheet as a Cape Open block (http://www.colan.org/). The key principles of stochastic modeling and the operation of the stochastic block in ASPEN are explained in the next section.

Figure 5 represents the biodiesel flow sheet used in this study.

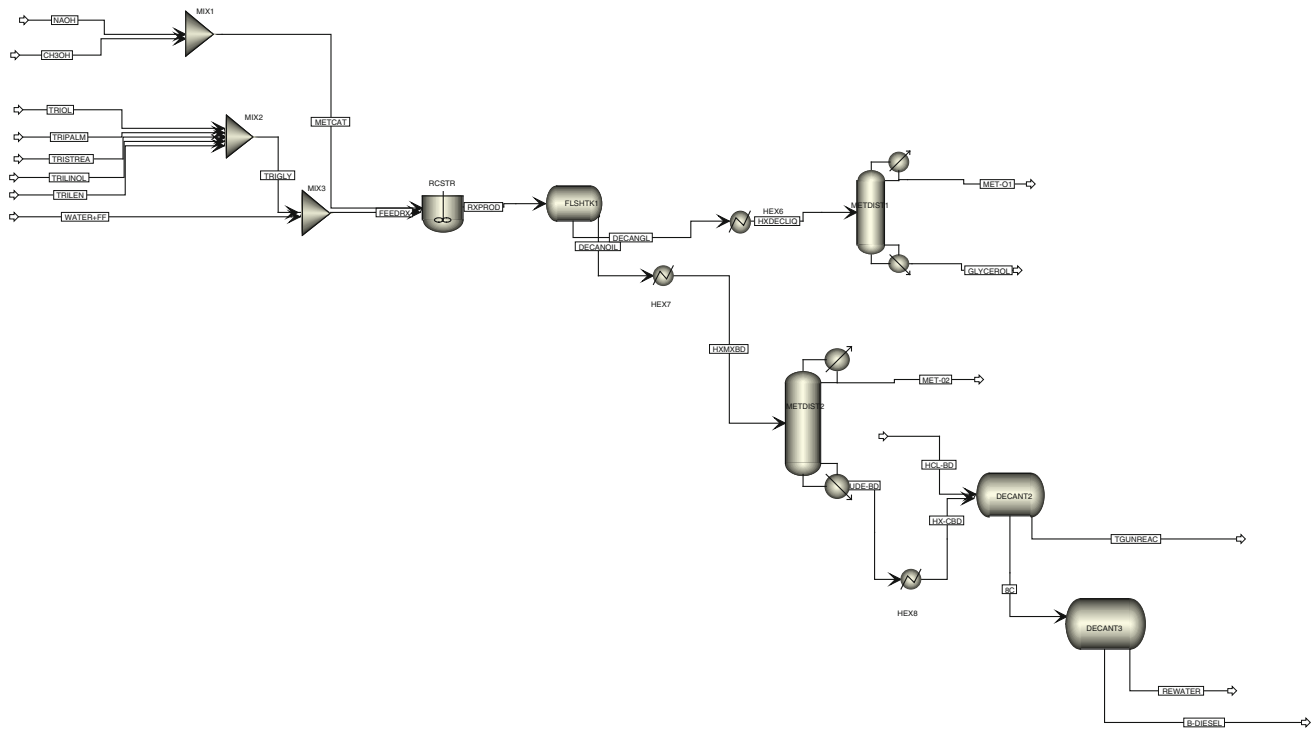

Fig. 5 ASPEN Biodiesel model

Stochastic modeling overview

Instead of dealing with only one possible reality of how the process might change with time, in the stochastic process, there is some indeterminancy in its future evolution described by probability distributions which implies that even if the initial condition is known, there are many possibilities the process might go to but some paths may be more probable and others less (Papoulis et al. 2001).

The ability to analyze uncertainties is important for processes the technical and economic parameters of which have not been well established. Uncertainties are important in comparing advanced system designs with baseline systems reflecting commercial technology. Sensitivity analysis can be carried out through a series of multiple runs. However, only one or two parameters at a time are varied in a simulation framework which may consists of a large number of independent variables. As a result important interactions may be overlooked (Diweker and Rubin 1991).

Diwekar et al. have described a stochastic modeling approach built around the ASPEN process simulator and have illustrated its applicability to a variety of simple and complex processes. (Diweker and Rubin 1991) To implement the stochastic modeling capability, ASPEN'S modular nature (consisting of unit operations module or blocks) was utilized. A unit operations block STOCHA characterizes the uncertainty in model input parameters in terms of probability distributions and analyzes there output on selected output variables.

Stochastic modeling approach involves the following procedure (Diweker and Rubin 1991)

1. Specifying uncertainty in key input parameters in terms of probability distributions.
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 advantages of using this stochastic modeling over sensitivity analysis are

1. The effect of several uncertainties can be analyzed in a single run in stochastic modeling compared with one or two for sensitivity analysis.
2. With large number of uncertain variables in sensitivity analysis, the volume of results makes their analysis cumbersome. But with stochastic modeling, the volume of results generated is generally very small.
3. Stochastic modeling results provide information about the likelihood of different outcomes in the form a probability distribution. Sensitivity analysis does not provide any information about the likelihood of different outcomes.

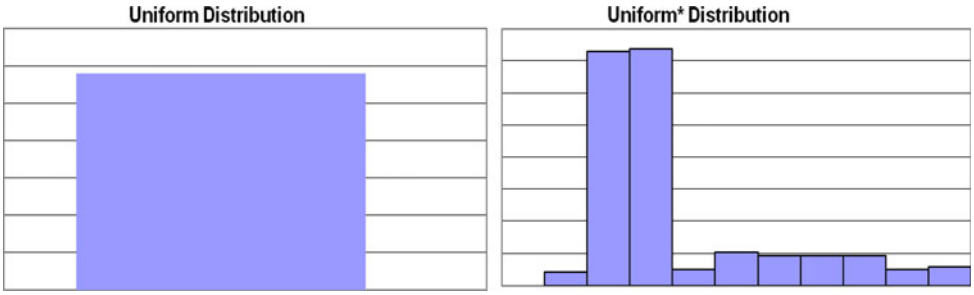

Fig. 6 Uniform and uniform* distribution

Table 1 Composition of various oils and fats (Linstromberg 1970)

Oil or fat	Tripalmitin 16:0	Triolein 18:0	Tristearin 18:1	Trilinolein 18:2	Trilenolenin 18:3
Soybean	6–10	2–5	20–30	50–60	5–11
Corn	8–12	2–5	19–49	34–62	Trace
Peanut	8–9	2–3	50–65	20–30	
Olive	9–10	2–3	73–84	10–12	Trace
Cottonseed	20–25	1–2	23–35	40–50	Trace
Hi linoleic safflower	5.9	1.5	8.8	83.8	
Hi oleic safflower	4.8	1.4	74.1	19.7	
Hi oleic rapeseed	4.3	1.3	59.9	21.1	13.2
Hi erucic rapeseed	3.0	0.8	13.1	14.1	9.7
Butter	24–26	10–13	28–31	1–2.5	0.2–0.5
Lard	28–30	12–18	40–50	7–13	0–1
Tallow	24–32	20–25	37–43	2–3	
Linseed oil	4–7	2–4	25–40	35–40	25–60
Yellow grease (typical)	23.24	12.96	44.32	6.97	0.67

4. Various sampling techniques area available with stochastic modeling for random sampling of input variables.

Stochastic simulation in ASPEN

The procedure of setting up stochastic modeling in ASPEN is follows (Subramanayan et al. 2007)

1. The STOCHA block is imported in ASPEN.
2. Dummy streams are attached to the STOCHA block.
3. Key input parameters required for the STOCHA block are
    a. Number of input uncertain variables
    b. Number of output uncertain variables
    c. Sampling technique
    d. Probability distribution function to represent the uncertainties in the input parameters.

The software provides a set of seventeen types of probability distribution functions for characterization of input variables. The probability distribution function used in this study was uniform*. This distribution is a modified form of uniform distribution. The key feature of uniform* distribution is that it the number of samples in each range can be listed. Figure 6 compares uniform distribution with uniform* distribution.

The input parameters for uniform* distribution are

1. No. of intervals.
2. No. of samples in each interval.
3. End points of each interval.

The sampling techniques available in with the STOCHA block are

1. HSS: Hammersley sequence sampling
2. LHS: Latin hypercube sampling
3. MCS: Monte Carlo Sampling

HSS Sampling technique is an efficient sampling technique and has been used in this study. Hammersley sampling generates inverts the Hammersley points (an optimal design for placing n points uniformly on a k-dimensional cube) to provide a representative sample for multivariate probability distributions (Diwekar et al. 1997).

Table 2 2008 US biodiesel production from various feedstocks (M311K 2008)

Feedstock source	MM lbs	Percentage
Soybean	3,314.7	66
Corn	189.6	4
Rapeseed	189.6	17
Lard	262.2	5
Tallow	252.8	5
Linseed oil	49.4	1
Yellow grease	113.6	2
Total	5,014.9	100

Characterization of uncertainties in biodiesel production

The uncertainties in biodiesel production are feedstock composition, methanol to oil ratio, reactor operating temperature.

Feedstock composition

Biodiesel feedstock is primarily composed of five different triglycerides. There are a variety of different feedstocks examples of which are soybean oil, palm oil, castor oil, etc. For each feedstock, the component triglyceride mass fraction also vary over a wide range. For example, as Table 1 shows, tripalmitin ranges is 6–10 % in soybean oil and 24–32 % in tallow. The mass fraction of triglyceride varies across a wide range in each feedstock and since there are wide range of available feedstock, the actual feedstock component at any given time is a random (stochastic) and can be represented by a probability distribution function within a range a values. The probability distribution used to represent the triglyceride uncertainties in feedstocks is uniform*. Uniform* distribution allows the capture of range of values in different feedstocks. This is better than a uniform distribution which will only the capture of range of values in a single feedstock source.

The method used to represent triglycerides with uniform* distribution is illustrated with the example of tripalmitin. The distribution of soybean oil in various oils for biodiesel production is shown in Table 1. Tripalmitin in

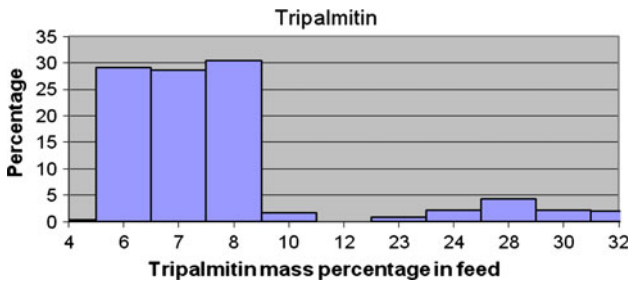

Fig. 7 Tripalmitin distribution

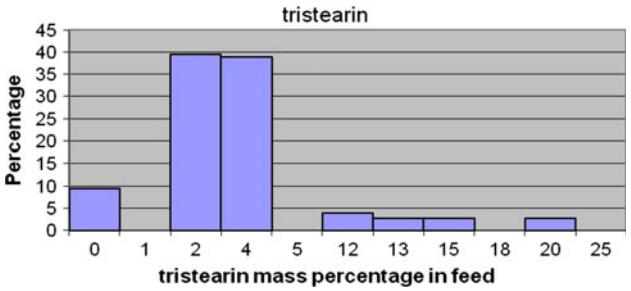

Fig. 8 Tristearin distribution

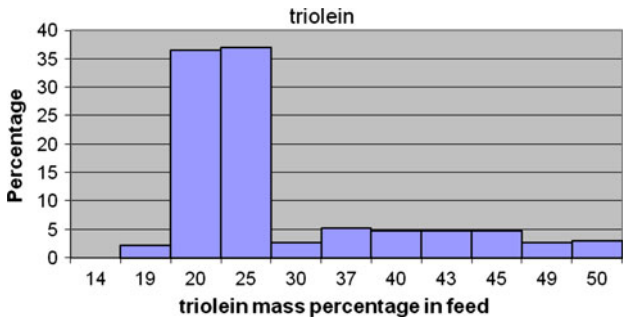

Fig. 9 Tristearin distribution

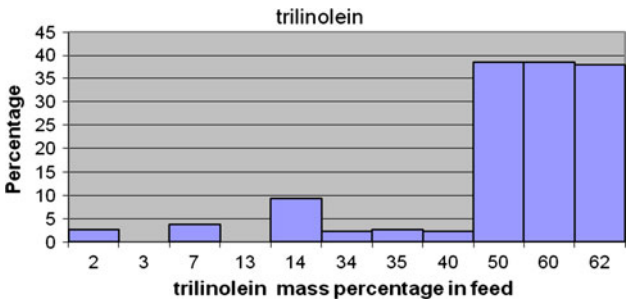

Fig. 10 Trilinolein distribution

soybean oil is 6–10 %, whereas 66 % of 2008 biodiesel production was through soybean oil. Tripalmitin range in corn oil is 8–12 %, whereas 4 % of 2008 biodiesel production was through soybean oil. The samples in the overlapping ranges are added together. Therefore, for a 100 samples, 66 samples will fall in the 6–8 range, 70 samples will fall in the 8–10 range, and 4 samples will fall in the 10–12 range. This procedure is followed for each triglyceride in all of the feedstock listed in the Table 2. The samples were normalized to 100. The following series of tables show the uniform* distribution for the five triglycerides (Figs. 7, 8, 9, 10).

Methanol to oil flow rate

Methanol is the most commonly used primary alcohol used in biodiesel production. Other alcohols such as isopropanol

Table 3 Methanol and reactor operating temperature distribution

Distribution of methanol in feed and reactor temperature			
Parameter	Distribution	Range	
Methanol	Uniform	1,200 lb/h	1,800 lb/h
Rx temp	Uniform	140 °F	200 °F

(IPA), ethanol, and butyl alcohol are also available. The separation process for separating the alcohols from biodiesel is similar. However, methanol cost per gallon is considerably less than ethanol, IPA, or butyl alcohols, and is therefore favored in the production process.

The stoichiometric methanol requirement is 3 mol of methanol per mole of triglyceride. Literature survey indicates that the mole ratio of methanol to oil flow rates depends on the production process, feedstock, operating parameters, and plant economics. The molar ratio of methanol to oil varies from 6:1 to 3:1 with a common value of 4:1 (Gerpen et al. 2004). Base-catalyzed process typically uses an operating mole ratio of 6:1 because it drives the reaction much closer to completion leading to higher yields (Gerpen et al. 2004). But, the unused reaction methanol must be recovered and recycled back into the process to minimize operating costs and environmental impacts. In addition, methanol is regulated under the recent EPA regulations for Miscellaneous Organic NESHAP (MON), and therefore production process must minimize methanol storage and usage. Therefore, during process design, considerations must be given to the molar ratio of methanol to oil because of its impact on (i) the transesterification reaction, (ii) process economics due the cost of methanol, difficulty of recovery and recycle, and (iii) environmental regulations. In this present study, methanol to oil ratio is treated as an uncertainty represented by a uniform distribution between molar ratio of 6:1 to 3:1. For input into the stochastic simulation model, the mole ratios are converted to methanol flow rate and defined by a uniform distribution between 1,200 and 1,700 lb/h. The distribution of methanol of methanol in the reactor feed is shown in Table 3.

Operating temperature of reactor

Transesterification of triglycerides is an endothermic reaction requiring heat. The selection of the operating temperature is based on reaction rate and single pass conversion, equipment design and size, and downstream separation requirement. A higher reactor operating temperature will lead to high conversion to methyl esters, but high temperature reactor vessel and more energy required. Further, high reactor operating temperature will cause methanol to begin to boil out from the reactant mixture leading to a pressure buildup in the reactor vessel. On the other hand, using a low reactor operating temperature will lead to a lower reaction rate, lower conversion, and larger reaction vessel. Therefore, the selection of the reactor operating temperature depends on various factors such as process economics, feedstock components, and equipment design. Temperature is considered as uncertain in this study because reaction rate changes with varying feedstock components. Stochastic modeling of reactor operating temperature will allow the process designer to consider its overall impact in relation to different feedstock operating conditions.

Literature survey indicates that the most common reactor operating temperature is 140 °F (Gerpen et al. 2004). Reactor operating temperatures as low as 77 °F and as high as 200 °F have been reported in literature. During this study, reactor operating temperature is represented by a uniform distribution and ranges between 140 and 200 °F. Very low operating temperatures have not been considered because even though they have been reported in literature, from a practical stand point, triglycerides have high freeze points and pipelines are normally electric traced to temperatures above 120 °F to keep lines from freezing. The distribution of reactor operating temperature is shown in Table 3.

Results and discussion

The results of stochastic simulation considered the impact of uncertainties in the overall biodiesel production process. The results of stochastic simulation were divided into two categories: (1) process efficiency for biodiesel production and (2) quality of biodiesel produced.

Process efficiency

The uncertainties characterized in the preceding section impact process efficiency. Process efficiency is based on the quantity of biodiesel produced at the end of the separation process. The quantity and type of triglycerides in the biodiesel feedstock impact the quantity of methyl esters in the final biodiesel. In addition, the methyl ester content determines if additional separation is required. To evaluate

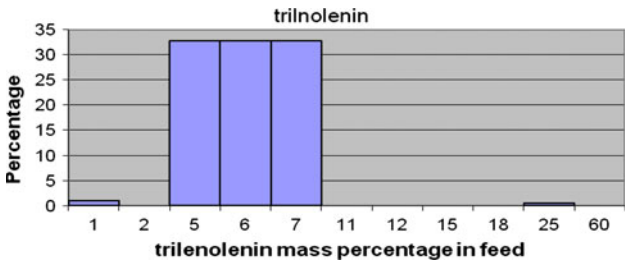

Fig. 11 Trilienolenin distribution

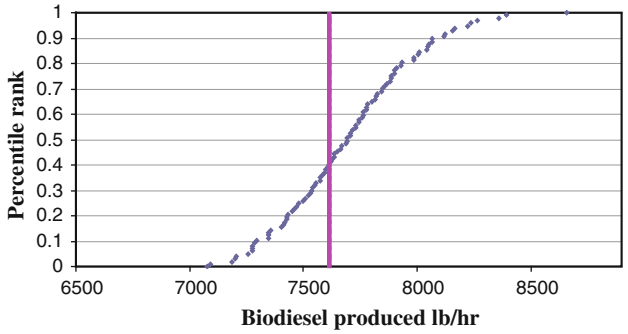

Fig. 12 Biodiesel production (lb/h)

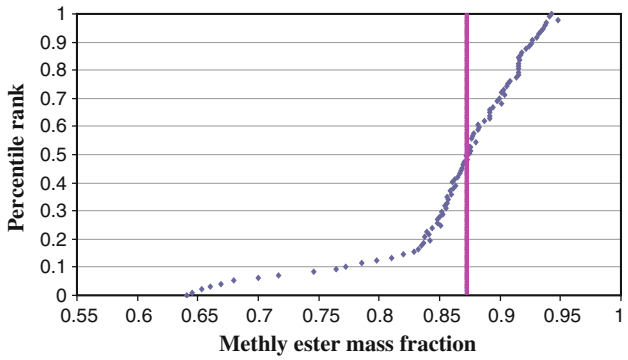

Fig. 13 Methyl ester mass fraction

the process efficiency, the stochastic model outputs were set as (1) quantity of biodiesel produced in lb/h and (2) methyl ester mass fraction in the biodiesel stream. These two output results are used to determine evaluate process efficiency as the single pass production of methyl esters based on a feed flow rate of 20,000 lb/h of feedstock.

The results of the propagation of uncertainties on the quantity of biodiesel produced are shown in Fig. 11. It should be noted that percentile rank is same as cumulative probability.

In addition to the quantity of biodiesel produced as determined by stochastic modeling, the vertical line in Fig. 12 shows the quantity of biodiesel produced for the deterministic case. The deterministic case is defined as the biodiesel production process without considering the uncertainties. The deterministic or base case is based on work done by El-Halwagi et al. (Myint and El-Halwagi 2008) The deterministic case is based on the component triglycerides of soybean oil.

The mass fractions of methyl ester in the biodiesel stream for both stochastic and deterministic case are shown in Fig. 13. Methyl ester mass fraction in the biodiesel stream determines the physical properties of the biodiesel and hence to determine if the product meets ASTM D 975 specification or if there is a need for blending with diesel. The results in Fig. 13 and Table 4 show a wide range for

Table 4 The range, mean, median and variance of the key output parameters

	Biodiesel produced (lb/h)	Triglyceride mass frac	Plant efficiency
Min	7,078	0.6412	13.3239
Max	8,659	0.9475	63.5068
Range	1,581	0.3063	50.1829
Mean	7,702	0.8604	41.0385
Median	7,694	0.8730	40.8610
Variance	94,002	0.0048	148.0740

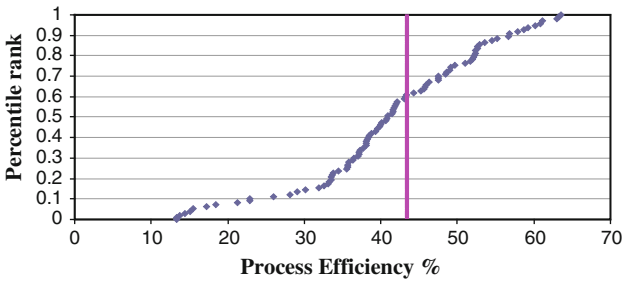

Fig. 14 Biodiesel process efficiency

the methyl esters in the biodiesel stream. Methyl ester mass fraction in the biodiesel stream have a wide range running from a low of 0.65 to a high of 0.95. Compared to the deterministic model, the stochastic model incorporates the uncertainties in feedstock and the results show that looking at the deterministic model by itself would not have given the process designer a complete picture of the methyl ester content in biodiesel stream. With the stochastic model, the process designer can more accurately determine if there is a need for additional blending.

The efficiency of the production process is described as the methyl ester content of the biodiesel per pound of feedstock to the reactor. The efficiency of the process is calculated through (methyl ester mass fraction $\times$ biodiesel lb/h)/mass of biodiesel feedstock to the reactor. The process efficiency is based on single pass conversion. Recycle streams are not considered.

Figure 14 shows the efficiency of the process and compares it to the deterministic case. Compared to the deterministic process efficiency of approximately 44 %, the stochastic model gives a range of process efficiency from 14 to 65 %. A wide range of process efficiency demonstrates that uncertainties in the production process can considerably change the process efficiency and in turn impact process operation, plant design, and economics. Further more, the broad range of process efficiency furthers that uncertainties in production process are not trivial and must be taken into consideration during the plant design stage.

Table 5 The effects of uncertainties on the properties of biodiesel

	Specific gravity	Specific heat (Btu/lb °F)	Kinematic viscosity (cSt)	Boiling point (°F)	Cetane number
Min	0.33	0.41	2.65	671	28.6
Max	0.80	0.60	3.73	711	46.3
Range	0.47	0.19	1.08	40	17.7
Mean	0.55	0.47	3.28	688	37.2
Median	0.55	0.47	3.20	688	37.6
Variance	0.01	0.00	0.09	80	16.7
Deterministic model	0.52	0.43	3.08	640	33.6
Conventional diesel	0.82–1.08		1.9–4.1		>40

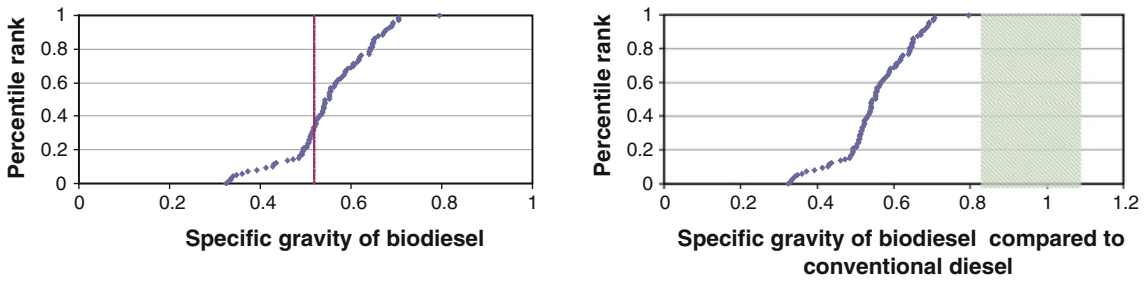

Fig. 15 Specific gravity of biodiesel obtained through stochastic modeling compared with deterministic case (*left*) and conventional diesel range represented by the *shaded area* (*right*)

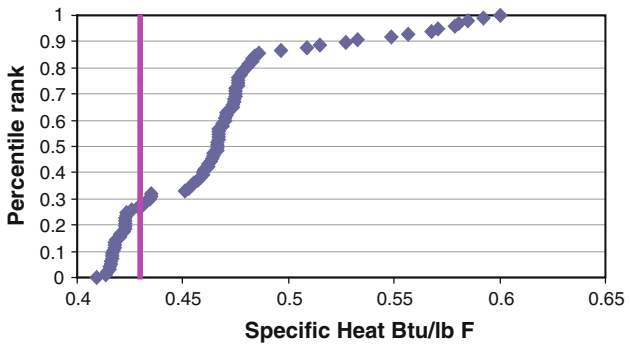

Fig. 16 Specific heat of biodiesel obtained through stochastic modeling compared with deterministic case

Biodiesel quality

The properties of biodiesel produced must meet or come close to meeting ASTM D975 specification for conventional diesel fuel. The specific properties evaluated in this model are specific gravity, specific heat, boiling point, viscosity, and cetane number. The physical properties of the biodiesel fuel effects the quality of the fuel and is a factor in making a determination if the fuel can be directly used in diesel engines or if blending is required. Due to the uncertainties in the biodiesel production process, the properties of the fuel fall in a range (Table 5). For the physical properties named above, a comparison is made between the properties calculated or evaluated through stochastic modeling and the values obtained through the deterministic model. In addition, the physical properties obtained through stochastic modeling are also compared with conventional diesel for the case of specific gravity, cetane number, and viscosity.

The specific and specific heat capacity of biodiesel are obtained through the ASPEN simulation model. Raoults law was used to determine the boiling point of biodiesel. The viscosity of the biodiesel was determined by Grunberg–Nissan used for determining the viscosity of liquid mixtures.

The specific gravity and specific heat of biodiesel are shown in the Figs. 15 and 16.

The specific gravity and specific heat capacity of biodiesel clearly show that the uncertainties in the feedstock components have an impact on the properties of the final product. Both specific gravity and specific heat have wide ranges compared to the deterministic model. The specific gravity of biodiesel shows that the uncertainties have a very significant impact on the specific gravity of biodiesel. However, both deterministic and stochastic values of specific gravity fall below the range for conventional diesel. This problem is circumvented by blending biodiesel with conventional diesel. An advantage of stochastic modeling is that the plant can define the uncertainty in the feed and use stochastic modeling to determine the degree of blending.

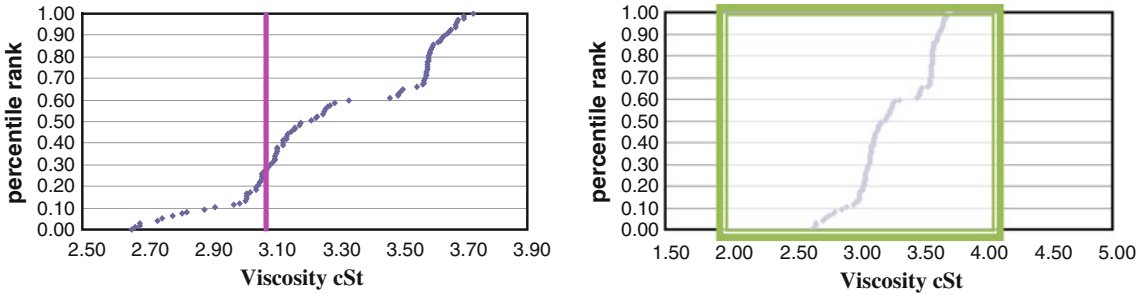

Fig. 17 Viscosity of biodiesel obtained through stochastic modeling compared with deterministic case (*left*) and conventional diesel range represented by the *shaded region* (*right*)

Table 6 Antoine equation coefficients for vapor pressure calculations

Antoine equation coefficients	MOLEATE 18:01	MPALMITE 16:00	MSTEARATE 18:00	MLINOLENATE 18:02	MLINOLENIN 18:03
A	9.9155	9.5714	9.3746	8.2175	8.1397
B	2,583.52	2,229.94	2,174.39	1,450.62	1,387.93
C	−96.15	−111.01	−131.23	−188.03	−196.16

Table 7 Cetane numbers for methyl esters

	MOLEATE 18:01	MPALMITE 16:00	MSTEARATE 18:00	MLINOLENATE 18:02	MLINOLENIN 18:03
CN	55	74.5	61.7	31.4	22.7

Using a stochastic model, quality control departments at plants can make judgments about the need for blending or further processing of biodiesel. In addition, uncertainty characterization can be narrowed down to a single feedstock such as soybean oil or tallow and then stochastic modeling can be used to determine the bandwidth for the physical properties leading to better control of product specification.

The viscosity of biodiesel is calculated by the Grunberg–Nissan equation. This equation is most suitable for computing the viscosity of binary liquid mixtures. Allen et al. (1999) have shown that this equation could be extended to mixtures of large number of components to predict the viscosity of biodiesel (Knothe 2005). Due to the similarity of the components in the mixtures, the components should not interact with each other and the thus are shown to behave in a similar manner as individual. The resulting viscosity of biodiesel is shown in the Fig. 17.

ASTM D975 specifies the acceptable properties of diesel. Stochastic modeling shows that the biodiesel properties fall within the specification for diesel. The results show that uncertainties in the production process do not have a considerable impact on the biodiesel viscosity.

The boiling point of biodiesel was determined by Antoine's equation constant for vapor pressure calculations and using Raoults law. Yuan et al. have compared the predicted vapor pressures of methyl esters and those reported through laboratory experiments. The difference between predicted and lab reported vapor pressures is 1 % (Yuan et al. 2005a, b). In addition, a sensitivity analysis indicated that the variation and feed stocks and uncertainty in feed stock components were the main factors that affected the predicted normal boiling points of the biodiesel fuels (Yuan et al. 2005a, b; Chang and Liu 2010). Raoults law is appropriate to determine the boiling point of the biodiesel fuel because the methyl ester components are large chain hydrocarbons with similar chemical structures and functional groups.

The vapor pressure coefficients for Antoine equations were used are shown in the Table 6 (Yuan et al. 2005a, b).

Cetane number (CN) represents the ignition quality of biodiesel under compression ignition conditions. In general, a compound that has a high octane number tends to have low CN and vice versa (Knothe 2005). The CN of fuel is related to the have ignition delay time. The ignition delay time is the time that passes between injection of the fuel into the cylinder and onset of ignition. The shorter the ignition delay time, the higher the CN and vice versa.

The simple mixing rule to predict the CN of biodiesel rule is (Knothe 2005)

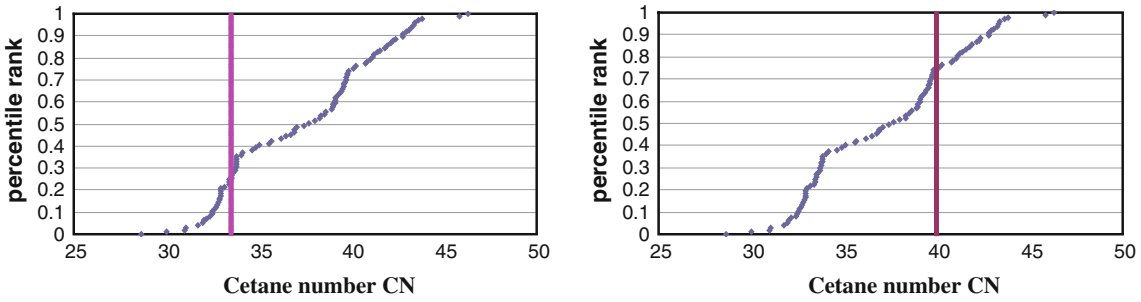

Fig. 18 Cetane number of range of biodiesel through stochastic modeling compared with the deterministic model (*left*) and minimum cetane number for diesel (*right*)

$$\mathrm{CN}_{\mathrm{biodieselfuel}} = X_i \sum \mathrm{CN}_{\mathrm{methyl\ ester}}$$

where X_i is the weight fraction of methyl ester and $\mathrm{CN}_{\mathrm{methyl\ ester}}$ is the CN of pure methyl ester. The CN of methyl esters are listed in the Table 7.

Only 25 % of the time, biodiesel fuel will meet the minimum cetane number value for conventional diesel (Fig. 18). Cetane number is an important factor in determining if additional blending is required. Biodiesel production process should be optimized to change the operating conditions of the reactors so as to favor conversion to high CN methyl esters. The triglycerides which favor low CN values will not be converted and can be separated out. This will improve the overall fuel characteristics.

Current biodiesel production processes have difficulty meeting ASTM D975 specification for diesel. An inability to meet the specification leads to quality control issues and sub par products. Future work of optimization under uncertainty will allow the process to become more efficient. In addition, the objective should be to run the process under much tighter specification control to bring the properties of fuel more in line with diesel specifications as this will reduce the need for large recycle streams, reduce the need for blending, and allow biodiesel to be sold as a completely independent fuel B100.

Conclusions

Stochastic modeling of biodiesel production process shows the affect of uncertainties on both the production process and properties of the finished product. Stochastic modeling of the production process allows the plant designer to design a plant which is more flexible in terms of being able to process various any type of feed. It has been found that uncertainties affect the plant performance as well as quality of product for biodiesel production significantly. This analysis will help in designing a plant which is more flexible and less affected by economic upswings and changes in commodity prices.

Acknowledgments We thank Vishwamitra Research Institute for their generous support in funding this research.

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