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Abstract

Crude glycerol is the byproduct of biodiesel production plant and the economic value of glycerol may affect the profitability of the biodiesel production plant. As the production rate of bioglycerol increases, its market values drop considerably. Therefore, conversion of bioglycerol into value-added products can reduce the overall cost, hence, leading to a more economical biodiesel production plant. In a direct carboxylation reaction, CO_2 reacts with glycerol to produce glycerol carbonate and water. This study presents a direct comparison of the economic analysis of the conventional biodiesel production plant and the possible next generation biodiesel-glycerol carbonate production plant. At the end of 15-year project, the net present value of the biodiesel-glycerol carbonate production plant is \$13.21 million higher than the conventional biodiesel plant. The stochastic model has predicted that the biodiesel-glycerol carbonate and conventional biodiesel production plants has about 30% and 63% chance of getting negative net present value, respectively. Heterogeneous catalyst, Ca_3La_1, is used for transesterification reaction to reduce separation steps in the biodiesel production process.

KEYWORDS: biodiesel, carboxylation of bioglycerol, n-dibutyltin(IV)oxide, heterogeneous catalyst, glycerol carbonate, economic analysis

1. Introduction

About 1 kg of glycerol is formed for every 10 kg of biodiesel produced (Nguyen and Demirel, 2010a). There is an inverse relationship between the production cost of biodiesel and the variations in the market value of bioglycerol. The production cost of biodiesel increases by \$0.008/gal for every \$0.01/lb reduction in glycerol selling price (Zheng et al., 2008). Therefore, economical utilization schemes of bioglycerol, such as carboxylation of bioglycerol to bioglycerol carbonate, can lead to a more economical biodiesel production.

Glycerol is a low toxicity polyol compound that can be used to produce polymers, ethers, hydrogen, bioglycerol carbonate and various fine chemical compounds by selective glycerol-based catalytic processes such as dehydration, hydrogenolysis, esterification, oxidation, and carboxylation (Chun-Hui et al., 2008; Olga et al., 2009). Direct carboxylation of carbon dioxide (CO_2) and bioglycerol to yield water and glycerol carbonate is one of the most environmentally friendly processes due to the consumption of the two by-products, CO_2 and bioglycerol (Aresta et al., 2006; George et al., 2009; Vieville et al., 1998). So far, only 35% conversion has been reported when the reaction proceeds at high pressure and high temperature (George et al., 2009). Therefore, development of a more robust catalyst for direct carboxylation is desirable (Dibenedetto et al., 2011).

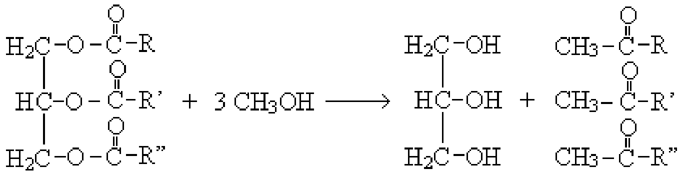
Glycerol carbonate is an intermediate chemical with many potential areas of application, such as, reactive protic solvent, a substitute for ethylene carbonate, propylene carbonate, cyclocarbonate derivatives, solvents for battery electrolyte, filming lubricants, filing plastifiers, agrosynthons, ingredients for cosmetics, and monomers for polymerization. It is also a novel component of gas separation membranes, coatings, paints and surfactants. It can act as a nonvolatile reactive solvent for several types of materials. In addition, it could serve as a source of new polymeric materials for the production of polycarbonates and polyurethanes (Chun-Hui et al., 2008; Olga et al., 2009).

2. Reactions

2.1 Transesterification

Utilizing conventional homogeneous catalyst such as NaOH or KOH in transesterification requires at least three distillation columns and produces large amounts of waste water (Lee and Saka, 2010; Zhang et al., 2003). Beside, the homogeneous catalyst is not reusable. Unlike homogeneous catalyst, heterogeneous catalyst can be regenerated and reused leading to reduction in separation steps and simplified biodiesel production process (Rajabathar and Ming, 2009; Yan et al., 2010; Zabeti et al., 2009). However, using heterogeneous catalyst requires higher alcohol/oil molar ratio (Di Serio et al., 2008; Sharma et al., 2010). In this study, lanthanum calcium oxide is used to catalyze the transesterification reaction, shown below

$$\text{Triglyceride} + \text{Methanol} \xrightarrow{\text{Catalyst}} \text{Bioglycerol} + \text{Biodiesel}$$

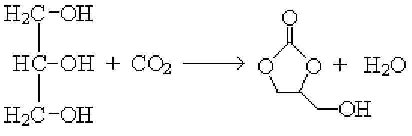


Lanthanum calcium oxides show high activity even in the presence of water, tolerating up to 3.6% on the weight basis of free fatty acid. They are highly stable, can be reused three times in a batch stirred reactor, and highly active for 14 days in a continuous fixed bed reactor, which may be suitable for industrial application (Yan et al., 2009; Yan et al., 2010a; Yan et al., 2010b). The optimum calcium to lanthanum molar ratio is 3 to 1 (Ca_3La_1) (Yan et al., 2010b). 94.3% conversion of oil is achieved when the reaction proceeds at 58 ^oC and 1 bar for 1 hour using 5% weight of Ca_3La_1 catalyst. The molar ratio of methanol to oil is 20:1 (Yan et al., 2009). In term of economic comparison, the cost of Ca_3La_1 is irrelevant since both plants use the same amount of catalyst and the net present value will increase proportionally.

2.2 Carboxylation

Under optimum conditions, maximum conversion for the direct carboxylation of bioglycerol in the presence of tin catalysts such as $n\text{-}Bu_2Sn(OMe)_2$ is around 7 to 10 percent (Aresta et al., 2006; Dibenedotto et al., 2011).

$$\text{Bioglycerol} + CO_2 \xrightarrow{\text{Catalyst}} \text{Bioglycerol carbonate} + \text{Water}$$



A conversion of 32.15 % can be achieved under supercritical CO_2 in the presence of zeolites and ion exchange resins (Vieville et al., 1998). However, excessive pressure results in higher equipment and operating costs. Finding a stable catalyst with a reasonable yield is crucial for reusing the catalyst and obtaining high conversion of bioglycerol. A recent study shows that 35% conversion is possible at 80 ^oC and 3.5 MPa using 1 mol% of *n*-dibutyltin(IV)oxide (n-Bu_2SnO) and methanol as solvent (George et al., 2009).

3. Base case and novel biodiesel production plants

3.1 Base case biodiesel production plant

The base case biodiesel production plant, shown in Fig. 1, utilizes methanol and triglyceride to produce fatty acid methyl ester (FAME) and glycerol using lanthanum calcium oxides as catalyst. Recycled and fresh methanol and oil are mixed in mixers M101 and M102 before they are fed into the reactor R101. Under 58 ^oC and 1 bar, 94.3% conversion of triglyceride is achieved (Yan et al., 2009). The reactor effluent, stream S3, containing mixture of catalyst, products, and unreacted reactants, is sent to separator SEP101 to recover Ca_3La_1. The outlet stream S4 enters flash drum F101 to recover the excess methanol. Fig. 2 shows that both the molar flow rates of methanol and glycerol in the recycle stream R3 increase as the temperature of the flash drum, F101, increases. The increase in the molar flow rate of glycerol in stream R3 is relatively sharper after 129 ^oC as indicated in Fig. 2b. Therefore, the operating temperature of the flash drum, F101, is set to 128.35 ^oC by a design specification block to control the flow rate of glycerol in stream R3.

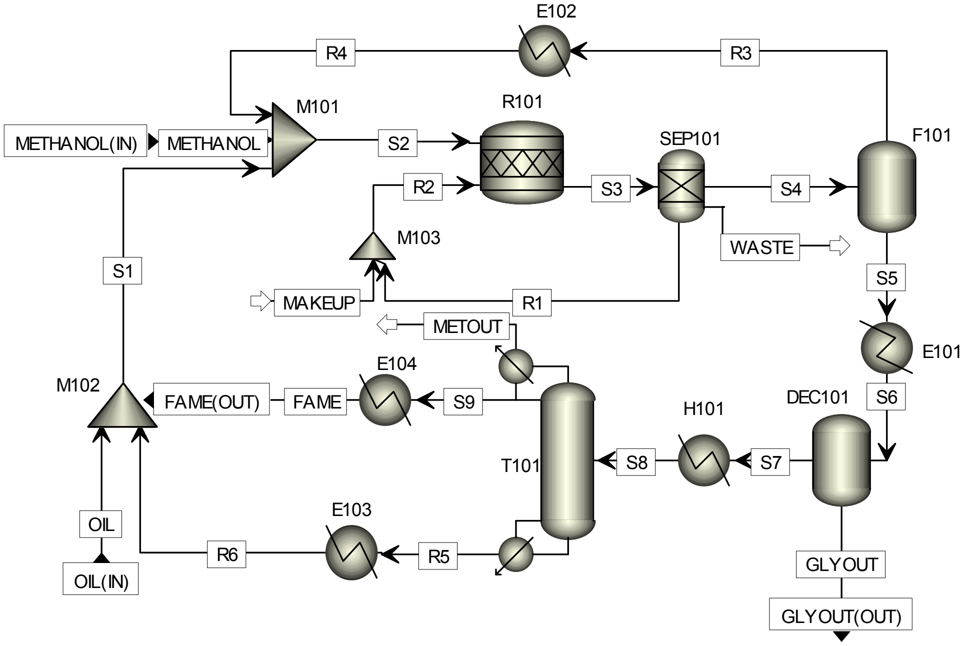


Fig. 1. Process flow diagram of the base case biodiesel production plant

The bottom product (S5) of the flash drum, F101, is cooled to 25 ^{o}C in cooler E101before it is sent to the decanter DEC101 to separate glycerol. Stream S7, containing unused oil, FAME, and methanol, is preheated to 300 ^{o}C before feeding to distillation column T101 to minimize exergy losses caused by the temperature gradient (Bandyopadhyay et al., 1998; Demirel, 2006; Nguyen and Demirel, 2010b; Nguyen and Demirel, 2011). Distillation column T101 operates with 5 equilibrium stages with a partial-vapor-liquid condenser and a kettle reboiler. The following two design specifications are used to control the top and bottom flow rates of the distillation column, T101. The first design specification sets the flow rate of FAME in stream R5 to 0.29 kmol/hr by varying the distillate flow rate. The second design specification sets the flow rate of FAME to 0.1 kmol/hr in stream METOUT by varying the distillate vapor fraction. The distillate flow rate is 20.96 kmol/hr and the distillate vapor fraction is 0.0129. The bottom stream containing mostly oil is recycled. The stream properties are summarized in Table 1, which is obtained by using Aspen Plus V7.2 with the thermodynamic model of UNIF-DMD. The activity coefficient model NRTL-RK model is used to estimate the vapor and liquid properties in column T101. Table 1 lists the streams used in the process flow diagram shown in Fig. 1. Overall, the base case biodiesel production plant consumes 704.88 kg/hr of methanol and 6074.47 kg/hr of oil to produce 6079.70 kg/hr of FAME and 664.55 kg/hr of crude bioglycerol as indicated in Table 1.

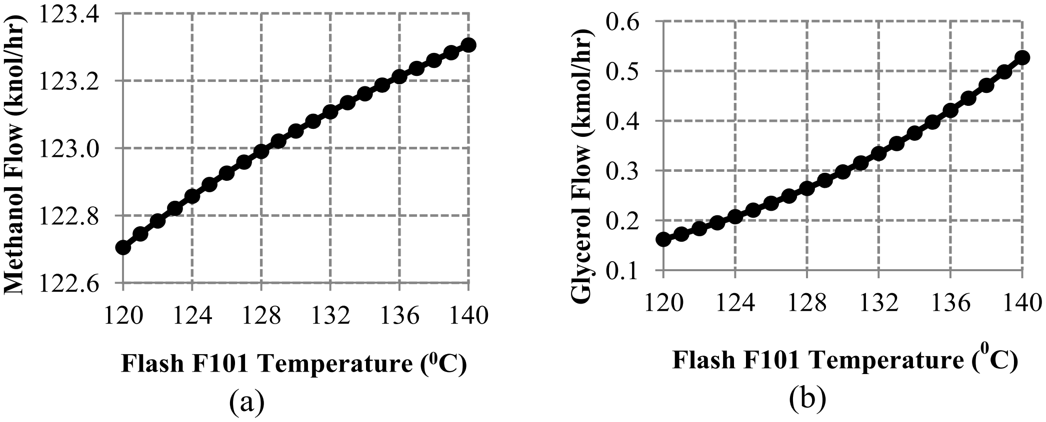


Fig. 2. Sensivity analysis of flash column F101 temperature on: (a) molar flow rate of methanol in stream R3; (b) molar flow rate of glycerol in stream R3.

Table 1

Streams properties of the base case biodiesel production plant shown in Fig. 1.

	FAME	GLYOUT	METHANOL	METOUT	OIL	R3	R4	R5	R6
Total Flow kg/hr	6079.70	664.55	704.88	35.10	6074.47	3999.72	3999.72	431.02	431.02
Temperature C	25.00	25.00	25.00	301.75	25.00	128.35	25.00	385.49	25.00
Pressure bar	1	1	1	1	1	0.5	1	1	1
Liquid Frac	1	1	1	0	1	0	1	1	1
Mass Flow kg/hr									
METHANOL	6.89E+00	3.36E+01	7.05E+02	5.44E+00	0.00E+00	3.94E+03	3.94E+03	3.98E-07	3.98E-07
OIL	4.94E+00	3.83E-12	0.00E+00	3.56E-03	6.07E+03	1.69E+01	1.69E+01	3.45E+02	3.45E+02
FAME	6.07E+03	6.10E-03	0.00E+00	2.96E+01	0.00E+00	1.67E+01	1.67E+01	8.60E+01	8.60E+01
GLYCEROL	3.66E-01	6.31E+02	0.00E+00	7.07E-03	0.00E+00	2.49E+01	2.49E+01	2.42E-05	2.42E-05
Mass Frac									
METHANOL	0.0011	0.0506	1.0000	0.1549	0.0000	0.9854	0.9854	0.0000	0.0000
OIL	0.0008	0.0000	0.0000	0.0001	1.0000	0.0042	0.0042	0.8005	0.8005
FAME	0.9980	0.0000	0.0000	0.8448	0.0000	0.0042	0.0042	0.1995	0.1995
GLYCEROL	0.0001	0.9494	0.0000	0.0002	0.0000	0.0062	0.0062	0.0000	0.0000

	S1	S2	S3	S4	S5	S6	S7	S8	S9
Total Flow kg/hr	6505.49	11210.09	11530.48	11210.09	7210.36	7210.36	6545.81	6545.81	6079.70
Temperature C	25.00	22.51	58.00	58.00	128.35	25.00	25.00	300.00	301.75
Pressure bar	1	1	1	1	0.5	1	1	1	1
Liquid Frac	1	1	1	1	1	1	1	1	1
Mass Flow kg/hr									
METHANOL	3.98E-07	4.65E+03	3.99E+03	3.99E+03	4.60E+01	4.60E+01	1.23E+01	1.23E+01	6.89E+00
OIL	6.42E+03	6.44E+03	3.67E+02	3.67E+02	3.50E+02	3.50E+02	3.50E+02	3.50E+02	4.94E+00
FAME	8.60E+01	1.03E+02	6.20E+03	6.20E+03	6.18E+03	6.18E+03	6.18E+03	6.18E+03	6.07E+03
GLYCEROL	2.42E-05	2.49E+01	6.56E+02	6.56E+02	6.31E+02	6.31E+02	3.73E-01	3.73E-01	3.66E-01
Mass Frac									
METHANOL	0.0000	0.4145	0.3458	0.3557	0.0064	0.0064	0.0019	0.0019	0.0011
OIL	0.9868	0.5742	0.0318	0.0327	0.0485	0.0485	0.0535	0.0535	0.0008
FAME	0.0132	0.0092	0.5377	0.5531	0.8575	0.8575	0.9446	0.9446	0.9980
GLYCEROL	0.0000	0.0022	0.0569	0.0585	0.0876	0.0876	0.0001	0.0001	0.0001

3.2 Novel biodiesel production plant

The novel biodiesel production plant contains two sections as shown in Fig. 3a. Section 1 (Fig. 3b) produces biodiesel and crude bioglycerol and Section 2 (Fig. 3c) produces bioglycerol carbonate and water. As seen in Fig. 3b, the locations of the decanter DEC101 and flash drum F101 are switched because of the separation of methanol from glycerol is undesirable since the methanol will be used as a solvent for the direct carboxylation of glycerol in Section 2. Section 1 of the novel biodiesel production plant uses 1050.98 kg/hr of methanol and 6062.43 kg/hr of oil to produce 6025.63 kg/hr of FAME and 4117.86 kg/hr of the stream, BY-PROD, containing 83.55%wt methanol as summarized in Table 2.

In section 2 (Fig. 3c), the stream GLYMET is mixed with the recycle stream R4 in mixer M201, and it is pressurized and heated to the reaction temperature before entering reactor R201. Stream GLYMET contains, by mass, 83.5% of methanol and 15.29% of glycerol, while stream R4 contains 96.6% glycerol. Carbon dioxide (CO_2) is compressed to 35 bars in compressor COM201 and cooled to 80 ^oC in cooler E201 before it is fed to reactor R201. The carboxylation reaction takes place at 80 ^oC and 3.5 MPa of CO_2 using methanol as a solvent and 1 mole percent of n-dibutyltin(IV)oxide as catalyst. The methanol/glycerol molar ratio of 11.41 (in stream S3) is used in this simulation while 11.38 is used by George et al., 2009. However, only 25% conversion is assumed in this simulation because of the ongoing research on the level of conversion achievable with the catalyst n-dibutyltin(IV)oxide (Dibenedetto et al., 2011). Separator SEP201 is used to separate the catalyst from the reactor outlet with 50% of recovered, treated, and recycled to the reactor.

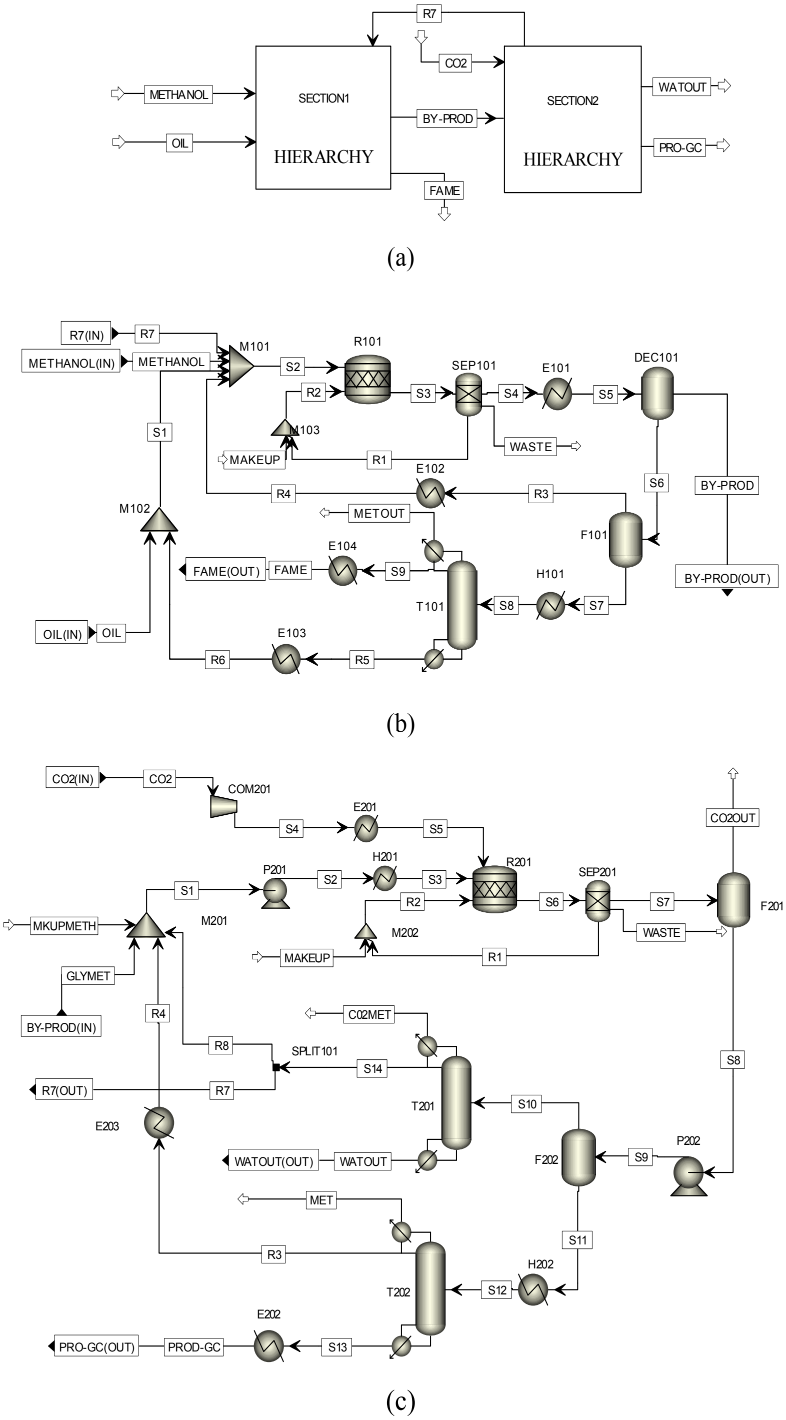


Fig. 3. (a) Hierarchy of the novel biodiesel production plant; (b) process flow diagram of Section 1 for biodiesel and bioglycerol production plant; (c) process flow diagram of Section 2 for bioglycerol carbonate production plant.

Design specification is set on flash drum F201 to control the flow rate of CO_2 by varying the column operating pressure. Flash drum F201 removes excess CO_2 operating at an absolute pressure of 0.181 bar. The bottom product of F201, stream S8, is pressurized to 1 bar in pump P202 upon entering flash drum F202 to separate water and methanol from glycerol and glycerol carbonate. The top product of T201, stream S10, containing methanol and water is fed to distillation column T201 at stage 5. Column T201 operates with 7 equilibrium stages with a kettle reboiler and a partial vapor-liquid condenser. The reboiler and condenser duties are 7,570.47 kW and 10,104.74 kW, respectively. The NRTL-RK model is used to predict the phase-equilibrium in distillation column T201. The distillate of T201, stream R7, contains high concentration of methanol, and is recycled to Section 1, while streams CO2MET and WATOUT are treated as waste.

The bottom product of flash column F202, stream S11, is preheated to 240^{o}C, and fed to stage 10 of distillation column T202 (Bandyopadhyay et al., 1998; Demirel, 2006; Nguyen and Demirel, 2010b; Nguyen and Demirel, 2011). The column T202 has 16 stages. The distillate, stream R3, contains mostly glycerol, which is recycled. The bottom product, stream S13, with a flow rate of 649.69 kg/hr and 93.54% on the weight basis is the glycerol carbonate. Glycerol carbonate properties are approximated based on the structural information obtained using the group contribution model of UNIF-DMD. The glycerol carbonate production section (Section 2) utilizes 273.74 kg/hr of carbon dioxide and 4117.86 kg/hr of glycerol and methanol to produce 649.69 kg/hr of glycerol carbonate and 209.51 kg/hr of water as shown in Table 3. Aspen Plus V7.2 is used for all the simulations.

Table 2
Streams properties of the novel biodiesel production plant (Section 1) shown in Fig. 3b.

	BY-PROD	FAME	METHANOL	METOUT	OIL	R3	R4	R5	R6
Total Flow kg/hr	4117.86	6025.63	1050.98	36.24	6062.43	571.64	571.64	443.01	443.01
Temperature C	25.00	25.00	25.00	297.11	25.00	158.26	25.00	386.58	25.00
Pressure bar	1	1	1	1	1	0.5	1	1	1
Liquid Frac	1	1	1	0	1	0	1	1	1
Mass Flow kg/hr									
METHANOL	3.44E+03	7.45E+00	1.05E+03	6.56E+00	0.00E+00	5.51E+02	5.51E+02	4.00E-07	4.00E-07
OIL	3.30E-04	4.95E+00	0.00E+00	3.87E-03	6.06E+03	4.16E+00	4.16E+00	3.57E+02	3.57E+02
FAME	4.26E+01	6.01E+03	0.00E+00	2.96E+01	0.00E+00	1.48E+01	1.48E+01	8.60E+01	8.60E+01
GLYCEROL	6.30E+02	4.63E-01	0.00E+00	8.80E-03	0.00E+00	1.52E-01	1.52E-01	3.02E-05	3.02E-05
WATER	3.45E+00	1.06E-03	0.00E+00	1.01E-03	0.00E+00	8.81E-02	8.81E-02	1.74E-11	1.74E-11
CO2	1.73E+00	1.35E-03	0.00E+00	1.13E-02	0.00E+00	1.30E+00	1.30E+00	1.05E-14	1.05E-14
Mass Frac									
METHANOL	0.8355	0.0012	1.0000	0.1811	0.0000	0.9641	0.9641	0.0000	0.0000
OIL	0.0000	0.0008	0.0000	0.0001	1.0000	0.0073	0.0073	0.8059	0.8059
FAME	0.0104	0.9979	0.0000	0.8182	0.0000	0.0259	0.0259	0.1941	0.1941
GLYCEROL	0.1529	0.0001	0.0000	0.0002	0.0000	0.0003	0.0003	0.0000	0.0000
WATER	0.0008	0.0000	0.0000	0.0000	0.0000	0.0002	0.0002	0.0000	0.0000
CO2	0.0004	0.0000	0.0000	0.0003	0.0000	0.0023	0.0023	0.0000	0.0000

	R7	S1	S2	S3	S4	S5	S6	S7	S8	S9
Total Flow kg/hr	3066.32	6505.45	11194.39	11514.15	11194.39	11194.39	7076.52	6504.88	6504.88	6025.63
Temperature C	63.61	25.00	37.36	58.00	58.00	25.00	25.00	158.26	300.00	297.11
Pressure bar	1	1	1	1	1	1	1	0.5	1	1
Liquid Frac	1	1	1	1	1	1	1	1	1	1
Mass Flow kg/hr										
METHANOL	3.06E+03	4.00E-07	4.66E+03	4.01E+03	4.01E+03	4.01E+03	5.65E+02	1.40E+01	1.40E+01	7.45E+00
OIL	2.13E-15	6.42E+03	6.42E+03	3.66E+02	3.66E+02	3.66E+02	3.66E+02	3.62E+02	3.62E+02	4.95E+00
FAME	5.56E-18	8.60E+01	1.01E+02	6.19E+03	6.19E+03	6.19E+03	6.14E+03	6.13E+03	6.13E+03	6.01E+03
GLYCEROL	2.52E-14	3.02E-05	1.52E-01	6.30E+02	6.30E+02	6.30E+02	6.24E-01	4.72E-01	4.72E-01	4.63E-01
WATER	3.46E+00	1.74E-11	3.54E+00	3.54E+00	3.54E+00	3.54E+00	9.02E-02	2.07E-03	2.07E-03	1.06E-03
CO2	1.75E+00	1.05E-14	3.04E+00	3.04E+00	3.04E+00	3.04E+00	1.31E+00	1.27E-02	1.27E-02	1.35E-03
Mass Frac										
METHANOL	0.9983	0.0000	0.4166	0.3479	0.3578	0.3578	0.0799	0.0022	0.0022	0.0012
OIL	0.0000	0.9868	0.5738	0.0318	0.0327	0.0327	0.0517	0.0556	0.0556	0.0008
FAME	0.0000	0.0132	0.0090	0.5372	0.5526	0.5526	0.8681	0.9421	0.9421	0.9979
GLYCEROL	0.0000	0.0000	0.0000	0.0547	0.0563	0.0563	0.0001	0.0001	0.0001	0.0001
WATER	0.0011	0.0000	0.0003	0.0003	0.0003	0.0003	0.0000	0.0000	0.0000	0.0000
CO2	0.0006	0.0000	0.0003	0.0003	0.0003	0.0003	0.0002	0.0000	0.0000	0.0000

Table 3

Streams properties of the glycerol carbonate production plant (Section 2) shown in Fig. 3c.

	CO2MET	CO2	CO2OUT	GLYMET	MET	MKUPMETH	PROD-GC	R3	R4	R7	R8	S1	S2
Total Flow kg/hr	164.94	273.74	173.49	4117.86	147.70	19.81	649.69	1334.84	1334.84	3066.32	4124.73	9597.25	9597.25
Temperature C	63.84	25.00	25.00	25.00	255.51	25.00	25.00	255.51	25.00	63.61	63.61	43.37	45.46
Pressure bar	1	1	0.18	1	1	1	1	1	1	1	1	1	35
Liquid Frac	0	0	0	1	0	1	1	1	1	1	1	1	1
Mass Flow kg/hr													
METHANOL	1.60E+02	0.00E+00	1.33E+02	3.44E+03	6.73E+01	1.98E+01	9.93E-06	3.72E+01	3.72E+01	3.06E+03	4.12E+03	7.62E+03	7.62E+03
FAME	3.25E-25	0.00E+00	3.90E-05	4.26E+01	1.66E-09	0.00E+00	3.57E+00	3.47E-08	3.47E-08	5.56E-18	7.47E-18	4.26E+01	4.26E+01
GLYCEROL	2.13E-20	0.00E+00	4.53E-05	6.30E+02	7.92E+01	0.00E+00	3.84E+01	1.29E+03	1.29E+03	2.52E-14	3.39E-14	1.92E+03	1.92E+03
WATER	4.42E-02	0.00E+00	6.48E-01	3.45E+00	8.63E-01	0.00E+00	2.36E-15	9.01E-02	9.01E-02	3.46E+00	4.65E+00	8.19E+00	8.19E+00
CO2	4.69E+00	2.74E+02	3.98E+01	1.73E+00	1.60E-02	0.00E+00	3.72E-24	2.82E-04	2.82E-04	1.75E+00	2.35E+00	4.09E+00	4.09E+00
GC	5.83E-23	0.00E+00	1.47E-05	0.00E+00	3.19E-01	0.00E+00	6.08E+02	8.27E+00	8.27E+00	1.94E-16	2.61E-16	8.27E+00	8.27E+00
Mass Frac													
METHANOL	0.9713	0.0000	0.7670	0.8355	0.4553	1.0000	0.0000	0.0278	0.0278	0.9983	0.9983	0.7935	0.7935
FAME	0.0000	0.0000	0.0000	0.0104	0.0000	0.0000	0.0055	0.0000	0.0000	0.0000	0.0000	0.0044	0.0044
GLYCEROL	0.0000	0.0000	0.0000	0.1529	0.5366	0.0000	0.0591	0.9659	0.9659	0.0000	0.0000	0.1999	0.1999
WATER	0.0003	0.0000	0.0037	0.0008	0.0058	0.0000	0.0000	0.0001	0.0001	0.0011	0.0011	0.0009	0.0009
CO2	0.0284	1.0000	0.2293	0.0004	0.0001	0.0000	0.0000	0.0000	0.0000	0.0006	0.0006	0.0004	0.0004
GC	0.0000	0.0000	0.0000	0.0000	0.0022	0.0000	0.9354	0.0062	0.0062	0.0000	0.0000	0.0009	0.0009

	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	WATOUT
Total Flow kg/hr	9597.25	273.74	273.74	9874.11	9870.99	9697.50	9697.50	7565.28	2132.23	2132.23	649.69	7191.05	209.51
Temperature C	80.00	448.82	80.00	80.00	80.00	25.00	25.05	140.00	140.00	240.00	315.53	63.84	90.96
Pressure bar	35	35	35	35	35	0.18	1	1	1	1	1	1	1
Liquid Frac	1	0	0	1	1	1	1	0	1	0.90	1	1	1
Mass Flow kg/hr													
METHANOL	7.62E+03	0.00E+00	0.00E+00	7.62E+03	7.62E+03	7.48E+03	7.48E+03	7.38E+03	1.04E+02	1.04E+02	9.93E-06	7.18E+03	3.89E+01
FAME	4.26E+01	0.00E+00	0.00E+00	4.26E+01	4.26E+01	4.26E+01	4.26E+01	3.91E+01	3.57E+00	3.57E+00	3.57E+00	1.30E-17	3.91E+01
GLYCEROL	1.92E+03	0.00E+00	0.00E+00	1.44E+03	1.44E+03	1.44E+03	1.44E+03	3.22E+01	1.41E+03	1.41E+03	3.84E+01	5.90E-14	3.22E+01
WATER	8.19E+00	0.00E+00	0.00E+00	1.02E+02	1.02E+02	1.01E+02	1.01E+02	1.00E+02	9.54E-01	9.54E-01	2.36E-15	8.11E+00	9.23E+01
CO2	4.09E+00	2.74E+02	2.74E+02	4.86E+01	4.86E+01	8.80E+00	8.80E+00	8.79E+00	1.62E-02	1.62E-02	3.72E-24	4.10E+00	6.70E-09
GC	8.27E+00	0.00E+00	0.00E+00	6.23E+02	6.23E+02	6.23E+02	6.23E+02	7.09E+00	6.16E+02	6.16E+02	6.08E+02	4.54E-16	7.09E+00
Mass Frac													
METHANOL	0.7935	0.0000	0.0000	0.7712	0.7715	0.7716	0.7716	0.9752	0.0490	0.0490	0.0000	0.9983	0.1855
FAME	0.0044	0.0000	0.0000	0.0043	0.0043	0.0044	0.0044	0.0052	0.0017	0.0017	0.0055	0.0000	0.1865
GLYCEROL	0.1999	0.0000	0.0000	0.1458	0.1458	0.1484	0.1484	0.0043	0.6599	0.6599	0.0591	0.0000	0.1537
WATER	0.0009	0.0000	0.0000	0.0103	0.0103	0.0105	0.0105	0.0133	0.0004	0.0004	0.0000	0.0011	0.4405
CO2	0.0004	1.0000	1.0000	0.0049	0.0049	0.0009	0.0009	0.0012	0.0000	0.0000	0.0000	0.0006	0.0000
GC	0.0009	0.0000	0.0000	0.0631	0.0632	0.0643	0.0643	0.0009	0.2890	0.2890	0.9354	0.0000	0.0338

4. Economic analysis

4.1 Deterministic model

Fix capital investment (FCI) is set equal to the grassroots cost (C_{GR}), which is approximated by the following equation (Turton et al., 2008)

$$C_{GR} = 1.68 \sum_{i=1}^{n} C^{o}_{Bm,i} \tag{1}$$

where $C^{o}_{Bm,i}$ is the bare module cost of equipment *i* at base conditions. The bare module costs of major equipment $C^{o}_{Bm,i}$ are estimated using the CAPCOST 2008 program and the chemical engineering plant cost index (CEPCI) of 580 for the year 2011 (O'Rourke et al., 2011).The FCI of the base case biodiesel plant is $17,429,160 and the cost of the novel biodiesel production plant is $29,276,352 as shown in Table 4. Land (L) and working capital (WC) are assumed equal to 5% and 20% of FCI, respectively. Cost of manufacturing (*COM*) without depreciation is given by (Turton et al., 2008)

$$COM = 0.18FCI + 2.73C_{OL} + 1.23(C_{UT} + C_{WT} + C_{RM}) \tag{2}$$

where the costs of utilities (C_{UT}), labor (C_{OL}), waste treatment (C_{WT}) and raw materials (C_{RM}) are shown in Table 4. Table 4 also shows the total cost of utilities provided by Aspen Plus V7.2 based on 8400 hr/year of the plant operation. The reported costs of low and medium pressure steam, cooling water, and electricity (Seider et al., 2009) are updated using the 2011 CEPCI of 580. Number of employee (N_{OL}) is estimated by (Turton et al., 2008)

$$N_{OL} = (6.29 + 31.7P^{2} + 0.23N_{np})^{0.5} \tag{3}$$

where P is the number of processing steps and N_{np} is the summation of number of equipment such as compressors, towers, reactors, heaters, and exchangers.

Table 4
Major cost factors of the biodiesel production plant.

	Base case	Novel
Fixed capital investment (FCI), \$	17,429,160.00	29,276,352.00
Land (L), \$ (5% of FCI)	871,458.00	1,463,817.60
Working capital (WC), \$ (20% of FCI)	3,485,832.00	5,855,270.40
Labor, \$/hr	30.00*	30.00*
Operating labor	14	16
Cost of labor (COL), \$	3,528,000.00	4,032,000.00
Cost of Electricity, \$/kW-h	0.0666	0.0666
Cost of cooling water, \$/ton	0.0202	0.0202
Cost of 1 bar steam, \$/kg	0.0024	0.0024
Cost of 35 bar steam, \$/kg	-	0.0166
Cost of utilities (CUT), \$	337,421.22	732,699.72
Waste treatment, \$/kg	0.37	0.37
Total cost of waste treatment, \$	108,123.23	1,042,564.12
Cost of methanol, \$/gal	0.75	0.75
Cost of oil, \$/barrel	93.00	93.00
Cost of CO_2, \$/kg	-	0.045
Cost of Ca_3La_1, \$/kg	150.00	150.00
Cost of n-Bu2SnO, \$/kg	-	40.00
Cost of raw materials, \$	47,247,426.66	48,846,767.63
Cost of manufacturing (COM), \$	71,431,043.26	78,542,202.08
Price of FAME, \$/gal	4.80	4.80
Price of crude glycerol, \$/kg	0.30	-
Price of GC, \$/kg	-	2.40
Revenue (R), \$/year	76,177,228.43	86,950,725.12
Taxation rate (t), %	35	35
Years of operation (n)	15	15
Years of depreciation (k)	5**	5**
Operational time, hr/year	8,400	8,400
Interest rate (i), %	5	5

* Updated using CEPCI = 580 (Turton et al., 2008); ** Less taxes paid when the project is depreciate as soon as possible.

The total cost of labor summarized in Table 4 is calculated based on 8400 hr/year of the plant operation. The cost of waste disposal is \$0.37/kg (Seider et al., 2009). The price of oil and methanol are \$93.0/barrel and \$0.75/gal, respectively (Tremain, 2011). The current selling price of products is presented in Table 4. With the inclusion of tax incentive and renewable index number, biodiesel producers can get up to \$2.80/gallon in addition to the market price of biodiesel (Geiver, 2011; Voegele, 2011), making the selling price of biodiesel approximately equal to \$4.80/gallon. Salvage (S) value is 0% of FCI (Turton et al., 2008). The useful life of the plants, taxation rate (t), depreciation and interest rate are also presented in Table 4.

The novel biodiesel production plant requires higher capital investment but generates higher revenue due to the value of glycerol carbonate. The book values (*BV*) are defined by

$$BV_k = FCI - \sum_{1}^{k} d_k^{MACRS} \tag{4}$$

and are evaluated using the modified accelerated cost recovery system (MACRS) depreciation method for 5 years (Turton et al., 2008).Cash flows (*CF*) is determined by (Turton et al., 2008)

$$CF = \left(R - COM - d_k^{MACRS}\right)\left(1 - t\right) + d_k^{MACRS} \tag{5}$$

where *R* is the revenue and *t* is the tax. In the deterministic model, based on the most likely economic data considered in Table 4, discounted cash flows (DCF) and cumulative discounted cash flows (CDCFs) are estimated. The plot of DCCFs versus years of operation yields the feasibility criteria of net present value (NPV), payback period (PBP), and rate of return (ROR) as shown in Table 5.

4.2 Stochastic model

In reality, over the years of operation, the prices of a product, labor, energy, and raw material change leading to fluctuations in the economic data considered in Table 4. Stochastic model uses probability analysis to quantify uncertainty of major economic data. Trapezoidal, normal, and lognormal density cumulative probability density function are often used to describe uncertainty in data. However, triangular cumulative probability function (*P(x)*) is used in this study to reduce calculation complexity (Turton et al., 2008)

$$P(x) = \frac{(x-a)^2}{(c-a)(b-a)} \qquad \text{for } x \le b \tag{6}$$

$$P(x) = \frac{(b-a)}{(c-a)} + \frac{(x-b)(2c-x-b)}{(c-a)(c-b)} \qquad \text{for } x > b \tag{7}$$

where a is the estimate of the lowest value, b is the most likely value and c is the estimate of the highest value. Since $P(x)$ (random number), a, b, and c are known, the above equation can be solved for x, which will yield two solutions. However, one will lie outside the interval (lower than a or higher than c) and will be disregarded.

Here, the uncertainties on the three major economic parameters of revenue (R), cost of manufacturing (COM), and fixed capital investment (FCI) are considered for comparison. Fixed capital investment may vary between -20% and +30%, the cost of manufacturing may vary in the range -10% to +10%, and the product price may vary from -20% to +5%. Random number generated from Rand() function in Microsoft's Excel program is used to assign the probability distributions as shown in Tables 6 and 7 for the base case and novel biodiesel plants, respectively.

5. Results and discussions

The market value of bioglycerol drop significantly due to its excess production as a by-product of the biodiesel production plant. Purification of glycerol in a small to medium scale biodiesel production plant is not an option due to high investment in separation units and low rate of return. As a result, direct conversion of glycerol into a value-added chemical, glycerol carbonate, reduces over production of crude glycerol and may improve the economics of the biodiesel plant as shown in Fig. 4. The process also consumes carbon dioxide, which is a renewable feedstock. In addition, glycerol carbonates has wide range of application, which can be used to produces valuable chemicals such as polymers, propylene carbonate, and cyclocarbonate derivatives.

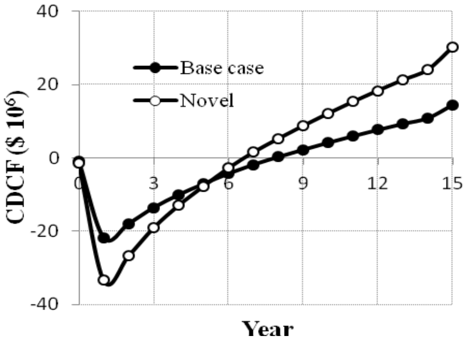


Fig. 4. Comparison of the cumulative discounted cash flow diagram of the base case and novel biodiesel production plants

Table 5
Discounted profitability criterion of the base case and novel plans.

	Base	Novel
Net present values (NPV, millions)	15.45	28.66
Rate of return (ROR, %)	15.58	16.56
Payback period (PBP, years)	4.7	4.4

Transesterification of triglyceride and methanol using solid catalyst requires higher methanol/oil molar ratio compared to homogeneous acid or base catalysts. Addition of glycerol carbonate production process directly uses of excess methanol as a solvent in the direct carboxylation reaction. The energy requirement for methanol recovery in flash column F101 is reduced considerably in section 1 of the novel biodiesel production plant compared with the base case biodiesel production plant. Streams R1, R3, and R5 are treated as tear streams in the biodiesel production section of both biodiesel production plants while streams R1, R3, and R7 are treated as tear streams in section 2 of the novel biodiesel production plant.

Fig. 4 shows the discounted cash flow diagrams generated using the deterministic model. As seen from Fig. 4, the net present value of the novel biodiesel plant is $13.21 million higher than the base case biodiesel plant at the end of 15-year project. Table 5 shows the results of the feasibility criteria of NPV, ROR, and PBP for the base case and novel operations obtained from the deterministic model. Any two of the criteria should be favorable for a feasible operation. The novel operation seems more favorable under current economic data considered in Table 4.

However, by taking into account of the uncertainties even on the values of R, COM, and FCI only to make predictions may lead to a more realistic economic assessment. Random distribution values of R, COM, and FCI are calculated by using equations 6 and 7. The values of NPV estimated from 20-point Monte-Carlo simulations are summarized in Tables 6 and 7. The cumulative probability curves (Fig. 5) is constructed by the order of the values of NPV from the lowest to highest. Fig. 5 illustrates that the novel biodiesel production plant has around 30% chance of having a NPV smaller than zero, while the base case plant has around 63% chance of having a NPV smaller than zero.

Tedious calculations can be avoided by using CAPCOST software to generate Monte Carlo simulation. Table 8 presents the uncertainties of some of the key parameters over the plant life. Fig. 6 presents the cumulative probability distributions obtained 1000-point Monte Carlo simulations for the values of NPV, ROR, and PBP values produced using CAPCOST software based on the uncertainties of parameters shown in Table 8. The results indicate that the novel biodiesel is about 33 percent more likely profitable compared to the base case biodiesel production plant. The lowest values of NPV for the base case and novel plants are -$81.9 and -$82.9 million, respectively, while the highest values of NPV for the base case and novel plants are $112.7 and $136.8 million, respectively.

Table 6

Results of the 20-Point Monte-Carlo Simulation of the base case biodiesel production plant (All $ figures are in millions).

Run	Rand(1)	R ($/yr)	Rand(2)	COM ($/yr)	Rand (3)	FCI ($)	NPV ($)
1	0.4832	72.78	0.8648	74.86	0.7464	19.26	-39.00
2	0.8738	76.96	0.3676	70.41	0.3678	17.29	16.09
3	0.6314	74.82	0.9560	76.46	0.1955	16.38	-34.24
4	0.1859	68.29	0.0163	65.58	0.4916	17.81	-7.11
5	0.6757	75.14	0.0293	66.02	0.5296	18.03	31.94
6	0.2345	69.19	0.5288	71.64	0.5153	17.96	-39.76
7	0.0934	66.15	0.6006	72.19	0.1780	16.27	-60.50
8	0.3741	71.36	0.6522	72.62	0.5246	18.00	-32.63
9	0.2332	69.17	0.1710	68.47	0.2289	16.58	-18.89
10	0.1942	68.45	0.3999	70.68	0.1244	15.89	-36.62
11	0.7793	75.98	0.7569	73.59	0.5049	17.91	-10.37
12	0.1901	68.37	0.2976	69.80	0.4911	17.81	-33.09
13	0.3307	70.74	0.6200	72.35	0.2198	16.53	-33.56
14	0.4769	72.70	0.7450	73.47	0.6261	18.53	-30.22
15	0.6388	74.87	0.3710	58.13	0.3146	17.03	3.30
16	0.6055	74.64	0.4477	71.05	0.4308	17.56	-2.32
17	0.7401	75.64	0.5897	72.10	0.2938	16.93	-2.32
18	0.2646	69.70	0.7430	73.45	0.9000	20.52	-50.40
19	0.1836	68.24	0.1916	68.71	0.6765	18.82	-27.87
20	0.3330	70.77	0.5435	71.75	0.9147	20.69	-32.89

R = Revenue, COM = Cost of manufacturing, FCI = Fixed capital investment, NPV = Net present value

6. Conclusions

This study shows that addition of glycerol carbonate production not only results in a more environmentally friendly process as it consumes renewable feedstock of carbon dioxide but it is also an economical process as it converts two by-products into a value-added bioproduct. Using deterministic model prediction, the net present value of the novel biodiesel production plant is $13.21 million higher than the base case biodiesel plant at the end of 15-year project. Also, stochastic model has predicted that addition of glycerol carbonate production may increase the probability of getting positive net present value by about 33% for the novel biodiesel plant.

Table 7

Results of the 20-Point Monte-Carlo Simulation of the novel biodiesel production plant (All $ figures are in millions).

Run	Rand(1)	R ($/yr)	Rand(2)	COM ($/yr)	Rand (3)	FCI ($)	NPV ($)
1	0.3616	81.25	0.3107	76.88	0.8722	34.01	-15.61
2	0.9395	88.91	0.9007	82.90	0.2910	28.42	-2.83
3	0.5543	84.81	0.5161	78.67	0.6955	31.80	-3.52
4	0.0984	75.66	0.6489	79.81	0.5412	30.38	-65.84
5	0.0059	71.05	0.3401	77.17	0.4723	29.78	-76.80
6	0.3584	81.20	0.1255	74.62	0.4199	29.42	1.83
7	0.8455	87.48	0.2510	76.25	0.0019	23.82	33.98
8	0.7484	86.42	0.5151	78.66	0.8084	33.10	5.46
9	0.1292	76.55	0.9478	83.86	0.7461	32.35	-87.50
10	0.5312	84.64	0.3417	77.18	0.2071	27.63	7.92
11	0.4873	83.13	0.8820	82.58	0.4310	29.50	-37.01
12	0.8294	87.28	0.6050	79.42	0.2673	28.21	9.46
13	0.8010	86.96	0.8657	82.33	0.5206	30.21	-12.41
14	0.6276	85.37	0.9898	85.27	0.9671	36.00	-45.12
15	0.8279	87.27	0.8576	82.20	0.2792	28.31	-7.47
16	0.8473	87.50	0.4284	77.96	0.0075	24.22	23.03
17	0.1160	76.18	0.6440	79.77	0.5091	30.11	-62.15
18	0.8731	87.84	0.0809	73.85	0.2332	27.89	48.54
19	0.5612	84.86	0.7552	80.90	0.3597	28.97	-15.12
20	0.2645	79.56	0.9014	82.91	0.7252	32.12	-62.88

R = Revenue, COM = Cost of manufacturing, FCI = Fixed capital investment, NPV = Net present value

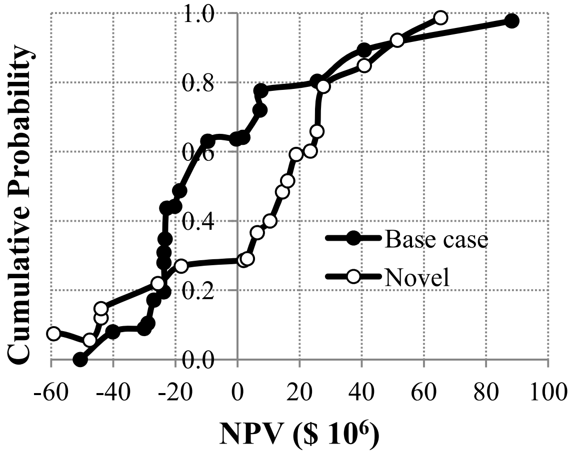
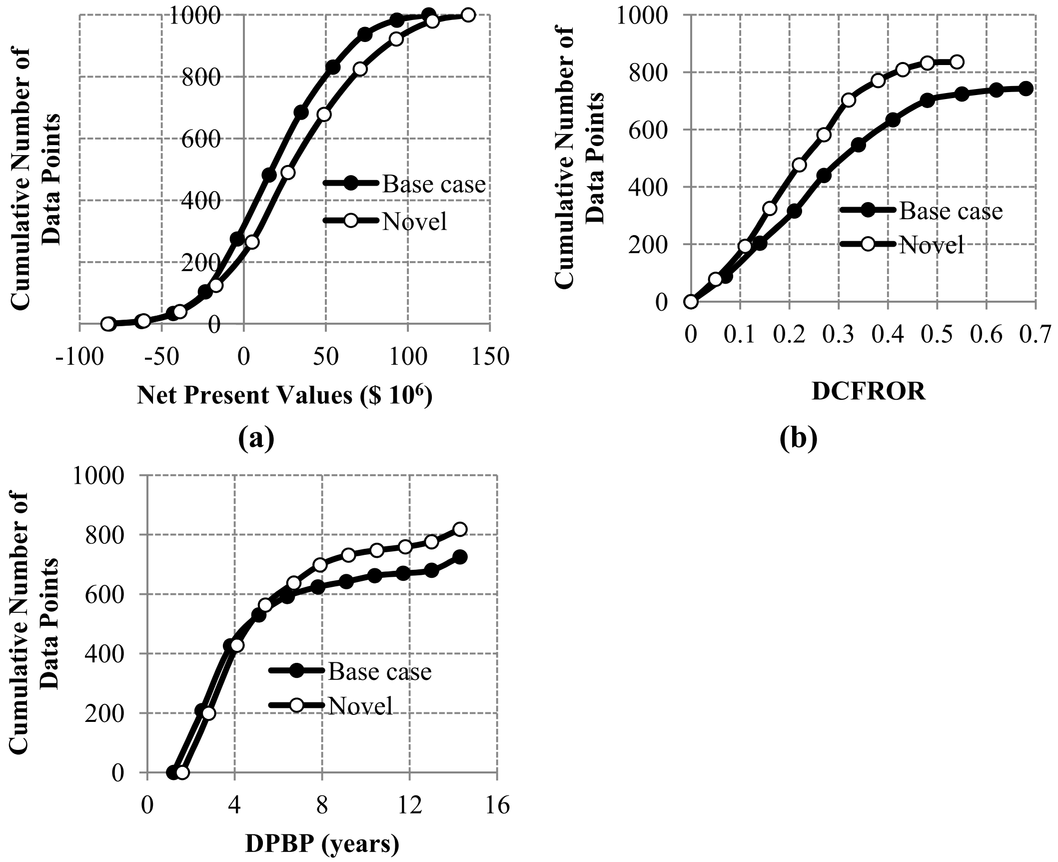


Fig. 5. Comparison of the cumulative probability of NPV obtained from the stochastic model using the uncertainties on revenue, fixed capital investment and cost of manufacturing only.

Table 8
Uncertainties on some key parameters

	Base case	**Novel**		
	Base value (b)	base value (b)	Lower limit (a)	Upper limit (c)
FCI	17,429,160	29,276,352	-20%	30%
Price of product, $	76,177,228	86,950,725	-10%	20%
Working capital, $	3,485,832	5,855,270	-10%	15%
Income tax rate, %	35	35	-5%	15%
Interest rate, %	5	5	-5%	5%
Raw material price, $	47,247,426	48,846,767	-10%	20%



(a) **(b)**

(c)

Fig. 6. 1000-point Monte Carlo simulation on; (a) net present values (NPV), (b) discounted cash flow rate of return (DCFROR), (c) discounted payback period (DPBP).

Nomenclature

a: estimate of the lowest value
b: most likely value
BV: Book values
c: estimates of the highest value
$C^{o}_{Bm,i}$: Bare module cost for equipment at base conditions
C_{GR}: Grassroots cost
$CDCF$: cumulative discounted cash flow
$CEPCI$: Chemical engineering plant cost index
CF: Cash flows
COM: Cost of manufacturing
d_{k}^{MACRS}: Modified accelerated cost recovery system depreciation method
DCF: Discounted cash flow
$DCFROR$: Discounted cash flow rate of return
$DPDP$: Discounted payback period
$FAME$: Fatty acid methyl ester
FCI: Fix capital investment
L: Land
$MACRS$: Modified accelerated cost recovery system
N_{np}: Summation of number of equipments
NPV: Net present value
N_{OL}: Number of employee
P: Number of processing steps
$P(x)$: Random number
PBP: Payback Period
ROR: Rate of return
S: Salvage
x: parameters such as R, COM, and FCI
WC: Working capital

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