

Techno-economic Analysis of Hydrodeoxygenation of Vegetable Oil for Production of Green Diesel Using Aspen Plus

A thesis Submitted to Indian Institute of Technology Hyderabad In Partial Fulfilment of the Requirements for The Degree of Master of Technology

By

Swarnalatha Mailaram

Under the guidance of

Dr. Sunil K Maity



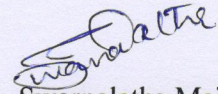
भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

**Department of Chemical Engineering
Indian Institute of Technology Hyderabad**

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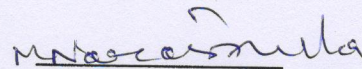


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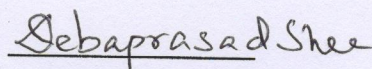
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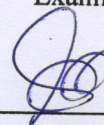
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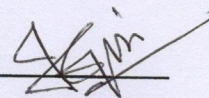
Dr. Narasimha Mangadoddy
Assistant Professor
Dept. of Chemical Engineering
Indian Institute of Technology Hyderabad
Examiner



Dr. Debaprasad Shee
Assistant Professor
Dept. of Chemical Engineering
Indian Institute of Technology Hyderabad
Examiner



Dr. Sunil Kumar Maity
Associate Professor
Dept. of Chemical Engineering
Indian Institute of Technology Hyderabad
Adviser

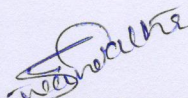


Dr. Jyotsnendu Giri
Assistant Professor
Dept. of Biomedical Engineering
Indian Institute of Technology Hyderabad
Chairman

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ABSTRACT

Techno-economic analysis is extremely important to demonstrate suitability of a process for potential forthcoming commercial developments. Hydrodeoxygenation (HDO) of triglycerides (vegetable oil, animal fat, waste cooking oil, and microalgal oil) is a potential approach for production of renewable diesel (green diesel) suitable for direct application in existing internal combustion engine thereby mitigating emission of harmful and greenhouse gases. The present work provides conceptual process design and economic feasibility analysis for HDO of inedible karanja oil for production of green diesel using Aspen plus. Two alternative routes for HDO of karanja oil were considered in the present work: direct and two-step HDO. In the present work, the karanja oil (non-databank compound) was considered as a mixture of triglycerides containing three same fatty acid groups in the structure. The physic-chemical properties of these non-databank triglycerides were included in Aspen Plus to regress property method. The regressed property method was then used for techno-economic analysis for various plant capacities. The unitary production cost of green diesel depends largely on plant capacity and cost of karanja oil. The unitary production cost of green diesel decreased significantly with increasing plant capacity and decreasing cost of karanja oil. 0.12 MMT karanja oil/annum was obtained as optimum plant capacity. The karanja oil was the largest cost contributing factor in the process of conversion of karanja oil to green diesel with share of up to 75% of unitary production cost of green diesel. Share of hydrogen was however only about 2% of overall production cost of green diesel. The propane and glycerol produced as co-product during direct and two-step HDO of karanja oil respectively generated significant amount of revenues for the respective process. The glycerol generated about 14% revenue for two-step HDO process compared to only about 1% by propane for direct HDO of karanja oil.

NOMENCLATURE

HDO Hydrodeoxygenation

CEPCI Chemical Engineering Plant Cost Index

MMT Million metric ton

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1. INTRODUCTION

According to global energy scenario, nearly 80% energy comes from fossil fuels and 90% organic chemicals are derived from petroleum. Total petroleum consumption in the world reached 91.19 million barrels per day in 2013 with an increase of 7.8% from 2005 (84.56 million barrels per day). Based on proved reserves so far, the crude oil is estimated to be exhausted in less than 50 years with the current rate of consumption [1]. Total energy consumption in the world reached 98.50 quadrillion Btu in 2014 with transportation fuels contribution of about 27% alone (Fig. 1) [2]. Moreover, large scale use of fossil fuels poses detrimental effects on the earth environment due to emission of toxic and greenhouse gases leading to global warming. Rapid depletion of fossil fuels reserves, continuous rise of demands for fuels and energy, escalation of oil price, and adverse impact on environment enforced paradigm shift of feedstock from fossil fuels to carbon neutral renewable resources for energy and organic chemicals.

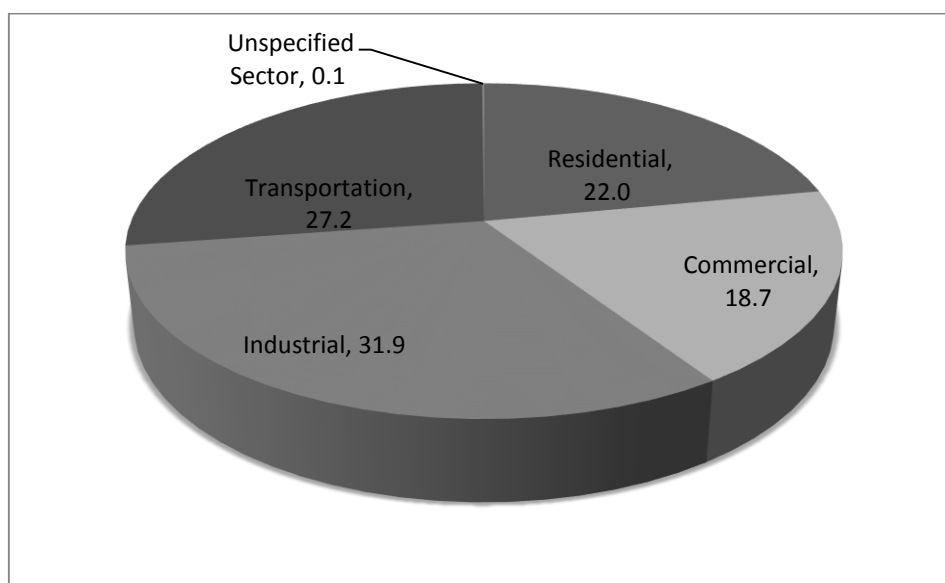


Fig. 1. Sector wise global energy consumption in 2014.

Biomass is considered as one of the most important renewable resource due to abundant availability, close simile with fossil fuels, and potential to provide all forms of energy, transportation fuels and organic chemicals. Biomass is generally classified into three broad classes: (a) triglyceride, (b) sugar and starchy, and (c) lingocellulosic [3]. The triglyceride biomass (vegetable oil, animal fat, waste cooking oil, and microalgal oil) is one of the most preferred feedstock due to structural simplicity, long hydrocarbon backbone with lesser

structural oxygen content compared to other biomass, and ease of processing to biofuels. Moreover, successful technological realization of microalgae will enable large scale availability triglyceride in near future without sacrificing agricultural land much [4]. Vegetable oils are in general two types: edible (for example, rapeseed, sunflower, soybean, palm oil etc.) and non-edible (for example, karanja, jatropha, mahua, neem etc.). Excessive use of edible vegetable oils for biofuels will eventually pose threat to food crisis and economic imbalance. The present work is thus based on non-edible karanja oil or pongamia oil extracted from seeds (29-39% oil content) of *Millettia pinnata* tree [5]. It is native to South and Southeast Asia and can tolerate drought and wide range of soils. Karanja oil was traditionally used for lighting of lamp in India. Estimates showed that India has annual production potential of about 20 million MT non-edible oil seeds with only a few percentage utilization with production potential of karanja oil alone being 0.2 million MT [6].

Transesterification of triglycerides with methanol in presence of alkali catalyst is most promising technology for production of fatty acid methyl ester (commonly known as biodiesel) for application as biofuel. However, high viscosity and pour/cloud point limits the application of biodiesel as blending with petro-diesel to the extent of 20% only for direct application in internal combustion engine. The biodiesel blended petro-diesel has however lower calorific value and hence lower fuel mileage compared to petro-diesel due to presence of structural oxygen. These attributes mainly deter widespread acceptability of biodiesel blended petro-diesel so far. Therefore, there is a strong need of producing hydrocarbon transportation fuels from triglyceride to enable direct application in internal combustion engine. The hydrocarbon fuels are additionally compatible with existing petroleum refinery infrastructure including storage and distribution network.

The hydrodeoxygenation (HDO) in presence of hydrogen at high pressure over supported metal catalyst is most promising technology for removal oxygen heteroatoms from triglycerides in the form of water, CO, and CO₂ [7][8][9]. HDO of triglyceride thus primarily produces diesel (or jet fuel range) fuels together with small quantity of gasoline commonly known as green diesel, green jet fuel, and green gasoline respectively. Green diesel has high energy density (44 MJ/kg), low specific gravity (0.78), good storage stability, better cold flow properties, and high cetane number (70-90) [10][11]. This attributes allow direct application of green diesel in existing internal combustion engine.

Several research and technological initiatives has been underway to make green diesel a commercial success in near future. Recently continuous one step process was demonstrated in a trickle-bed reactor using Pt/SAPO-11-Al₂O₃ as catalyst for production of green diesel from

soybean oil at 375–380 K and 30 bar with LHSV of 1 h⁻¹ [12]. Linear paraffins, branched paraffins, naphthenes, and mono-aromatics were observed as products suitable as high quality components for diesel. Liu and his co-workers reported high yield (80%) of liquid hydrocarbons with high isomerization selectivity (80%) and excellent stability during HDO of palm oil over nano-sized SAPO-11 supported nickel catalyst in single step [13]. Krar and his co-workers reported high normal and isoparaffin yield with cetane number more than the specified limit of diesel during HDO of sunflower oil over CoMo/Al₂O₃ [14].

UOP in collaboration with Eni S.p.A. (Italy) developed two-step Ecofining process for HDO of vegetable oils (soybean, palm, and rapeseed oils) into high cetane green diesel enriched with isoalkanes [15]. In this process, vegetable oil was mixed with hydrogen, heated to 473–573 K, and fed into a HDO reactor loaded with sulfided catalyst. The hydrocarbons were subsequently hydroisomerized in another reactor to produce green diesel with properties similar to petrodiesel. UOP has also developed green jet fuel process which is based on traditional refining hydroprocessing technology. Hydrogen is added to feedstock to remove oxygen and then refining the product for the required specifications to be met [16]. Neste Oil developed NExBTL technology to produce renewable diesel with cetane number of 84-99 and cloud point as low as 240 K [17].

Economic analysis is extremely useful to evaluate and compare feasibility of various alternative routes and estimate cost of production to inspire commercialization of a process. Realizing the importance several techno-economic analyses were reported in the past on production of biodiesel. Tao and Aden reported production cost of \$2.55/gallon biodiesel from soybean oil in 2007 USD (\$2.8135/gal in 2015 USD according to CPECI) for plant capacity of 45MM gal/year biodiesel [18]. Despite significant research progress, limited studies are available on techno-economic and life cycle analysis for HDO of triglycerides for production of green diesel. Life cycle analysis showed that tallow green diesel has life cycle GHG emissions as low as 2% of petrodiesel emissions [10]. Davis and his co-workers reported production cost of \$9.84/gal of diesel and \$20.53/gal of diesel from autotrophic microalgae via open pond and photo-bioreactor respectively [19]. From the above discussion, it is quite clear that techno-economic analysis for HDO of karanja oil was not reported so far in open literature. A novel methodology was thus developed in the present work for process design and economic feasibility analysis of HDO of karanja oil using Aspen Plus.

In general, HDO of karanja oil can be carried out using two possible approaches as shown in Fig. 2. In the first approach (hereafter called direct HDO), neat karanja oil undergoes direct HDO producing green diesel with propane as co-product. In the second approach, the karanja

oil is first hydrolysed to corresponding fatty acids and glycerol in presence of small amounts of sulphuric acid or more usually zinc oxide. The fatty acids obtained from hydrolysis of karanja oil subsequently undergo HDO for production of green diesel. This process is referred as two-step HDO of karanja oil throughout the thesis. The resent work provides a systematic comparison of techno-economics of both processes.

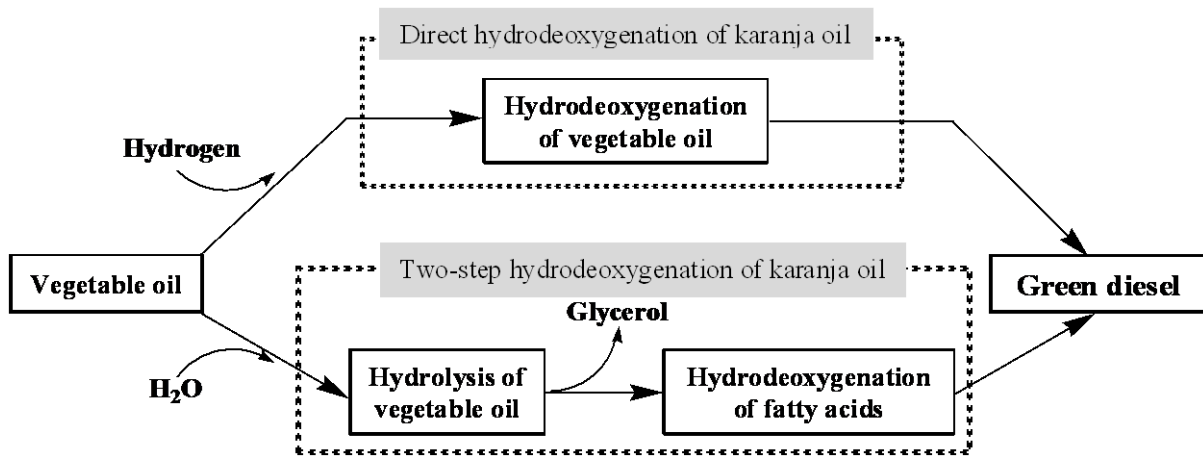


Fig. 2. Possible hydrodeoxygenation routes for production of green diesel from vegetable oil.

2. OBJECTIVES

Developments of a conceptual process for HDO of non-edible vegetable oil for production of hydrocarbon fuels (green diesel) and evaluation of cost for production of green diesel are main objectives of the whole project. The more specific objectives of the project are as shown below.

1. To develop possible alternative processes using Aspen Plus for HDO of non-edible karanja oil as feedstock for production of green diesel.
2. Economic evaluation of various processes using appropriate models available in Aspen Plus.
3. To compare the cost of production for various processes to obtain economically most attractive process.

3. METHODOLOGY

3.1 Strategy of handling non-databank components in Aspen Plus

Conceptual design and economic feasibility analysis is extremely important prior to commercialization of a process. In the present work, the conceptual process design for HDO of karanja oil together with material and energy balance was developed using Aspen Plus®, Aspen Tech™. The process design using Aspen Plus however requires pure components information. On the other hand, vegetable oil (fatty acid ester of glycerol) is in general composed of three fatty acids bonded with glycerol by ester bond. The three fatty acids present in a triglyceride molecule may or may not be the same and expected to be distributed statistically among three hydroxyl group of glycerol based on fatty acid composition of the vegetable oil. It is therefore quite obvious that vegetable oil is a complex mixture of wide range of triglycerides. Handling such a wide range of chemical compounds in Aspen Plus is really challenging. For simplicity of analysis, vegetable oil is considered as mixture of triglycerides with three identical fatty acid groups in the structure [20]. On the other hand, fatty acid composition of vegetable oils generally varies significantly depending on types, source, and geographical origin. However, most of the vegetable oil are commonly composed of C₈-C₂₄ fatty acids (both saturated and unsaturated) with majority of them being C₁₆ and C₁₈ fatty acids. Based on available information in open literature, it was observed that karanja oil is generally composed of palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), and behenic acid (C22:0) [21]. Therefore, in the present work, karanja oil is considered as a mixture of tripalmitin, tristearin, trioleate, trilinolein, and tribehenin (Table 1).

Table 1. Fatty acid composition of karanja oil.

Fatty acids	Structure	Formula	wt%
Palmitic	C16:0	C ₁₆ H ₃₂ O ₂	11.3
Stearic	C18:0	C ₁₈ H ₃₆ O ₂	8.4
Oleic	C18:1	C ₁₈ H ₃₄ O ₂	54.4
Linoleic	C18:2	C ₁₈ H ₃₂ O ₂	15.8
Arachidic acid	C20:0	C ₂₀ H ₄₀ O ₂	3.7
Behenic acid	C22:0	C ₂₂ H ₄₄ O ₂	6.4

Tripalmitin, tristearin, trioleate, trilinolein, and tribehenin are however non-databank compounds of Aspen Plus. For handling non-databank compound, several physicochemical properties (including structure, molecular weight, boiling point, vapour pressure, standard

enthalpy, standard Gibb's free energy, and heat capacity) needs to be incorporated in Aspen Plus prior to process simulation [22][23]. Some of the physicochemical properties of these triglycerides method were obtained from different literatures as shown in [Table 2](#). The temperature dependent properties such as heat capacity and vapor pressure of some of these triglycerides available in open literatures are reported in [Table 3](#) and [Table 4](#) [24][25][26]. The property methods used in the present work (Soave-Redlich-Kwong, SRK) were first regressed using available physicochemical properties of the considered triglycerides [23]. The regressed property methods were then used for all subsequent simulations.

Table 2. Physicochemical properties of various pure triglycerides.

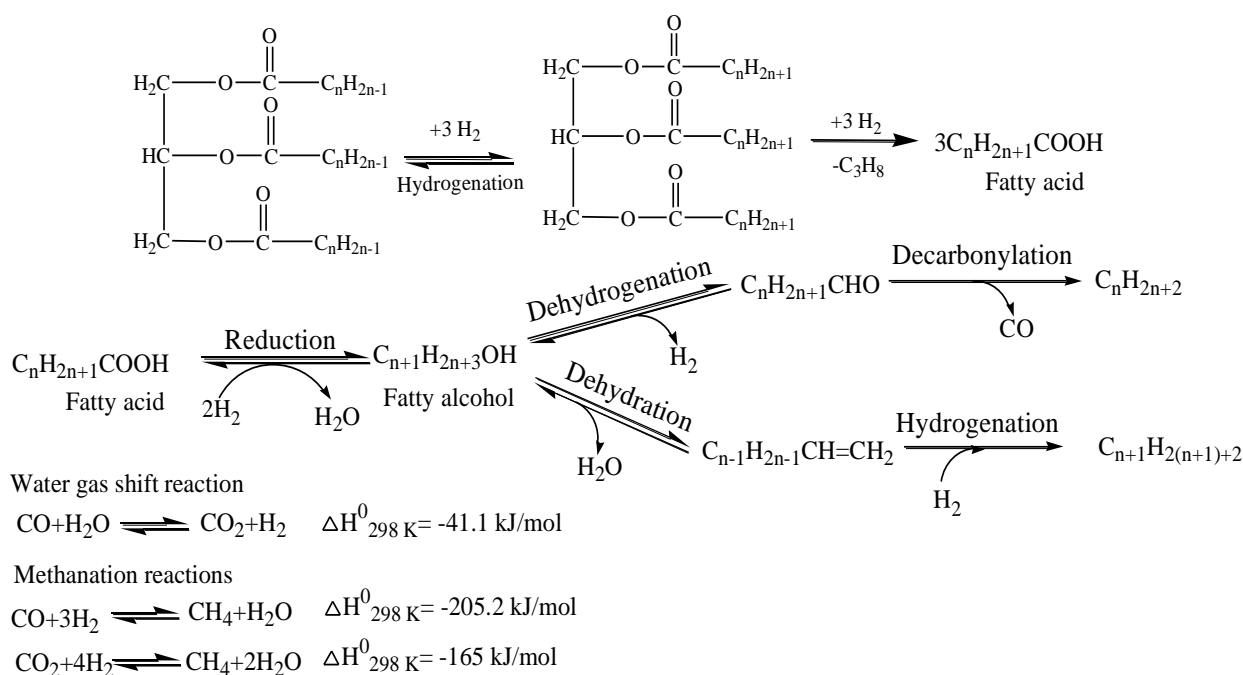
Triglyceride	Chemical structure	Normal boiling Point, K	Specific gravity	Vapour pressure at 298 K, mmHg	ΔH_0^{vap} , kJ/kmol	ΔG_0^{vap} , kJ/kmol	Ref.
Tricaprylin	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_7\text{H}_{15} \\ \\ \text{CH} - \text{O} - \text{COC}_7\text{H}_{15} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_7\text{H}_{15} \end{array}$	781.15	0.954	6.69×10^{-2}	1.16×10^5	3.471×10^4	www.chemnet.com
Tricaprin	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_9\text{H}_{19} \\ \\ \text{CH} - \text{O} - \text{COC}_9\text{H}_{19} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_9\text{H}_{19} \end{array}$	851.75	0.949	6.7×10^{-11}	1.246×10^5	4.355×10^4	www.lookchem.com
Trilaurin	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_{11}\text{H}_{23} \\ \\ \text{CH} - \text{O} - \text{COC}_{11}\text{H}_{23} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_{11}\text{H}_{23} \end{array}$	916.45	0.935	1.94×10^{-13}	1.377×10^5	5.371×10^4	www.chemnet.com
Trimyristin	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_{13}\text{H}_{27} \\ \\ \text{CH} - \text{O} - \text{COC}_{13}\text{H}_{27} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_{13}\text{H}_{27} \end{array}$	952.42	0.885	5.55×10^{-4}	1.478×10^5	6.272×10^7	www.pubchem.com
Tripalmitin	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_{15}\text{H}_{31} \\ \\ \text{CH} - \text{O} - \text{COC}_{15}\text{H}_{31} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_{15}\text{H}_{31} \end{array}$	1086	0.916	5.55×10^{-4}	1.608×10^5	7.22×10^7	www.pubchem.com
Tristearin	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_{17}\text{H}_{35} \\ \\ \text{CH} - \text{O} - \text{COC}_{17}\text{H}_{35} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_{17}\text{H}_{35} \end{array}$	1033	0.909	5.4×10^{-17}	1.675×10^5	7.776×10^7	http://toxnet.nlm.nih.gov/
Triolein	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_{17}\text{H}_{33} \\ \\ \text{CH} - \text{O} - \text{COC}_{17}\text{H}_{33} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_{17}\text{H}_{33} \end{array}$	1120	0.911	5.15×10^{-17}	-	-	www.pubchem.com
Trilinolein	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_{17}\text{H}_{31} \\ \\ \text{CH} - \text{O} - \text{COC}_{17}\text{H}_{31} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_{17}\text{H}_{31} \end{array}$	1089.65	0.933	5.09×10^{-21}	-	-	www.lookchem.com
Triarachidin	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_{19}\text{H}_{39} \\ \\ \text{CH} - \text{O} - \text{COC}_{19}\text{H}_{39} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_{19}\text{H}_{39} \end{array}$	1136.73	0.904	1.2×10^{-23}	-	-	www.chemblink.com
Tribehenin	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{COC}_{21}\text{H}_{43} \\ \\ \text{CH} - \text{O} - \text{COC}_{21}\text{H}_{43} \\ \\ \text{CH}_2 - \text{O} - \text{COC}_{21}\text{H}_{43} \end{array}$	1184.95	0.899	2.65×10^{-24}	-	-	www.chemnet.com

Table 3. Heat capacity of triglycerides [22].

Tripalmitin		triolein		tristearin	
Temperature, °C	Heat capacity, J/g-K	Temperature, °C	Heat capacity, J/g-K	Temperature, °C	Heat capacity, J/g-K
80	2.1772	60	2.0827	80	2.1772
100	2.2267	80	2.1227	100	2.2267
120	2.2762	100	2.1627	120	2.2762
140	2.3257	120	2.2027	140	2.3257
160	2.3751	140	2.2427	160	2.3751
180	2.4246	160	2.2827	180	2.4246
		180	2.3227		

Table 4. Vapour pressure data for triglycerides [24].

Temperature, K	Tristearin, bar	Tripalmitin, bar
303	0.026484	0.052888
313	0.026674	0.052891
323	0.026676	0.052894
333	0.026677	0.052897
343	0.026678	0.0529
353	0.02668	0.052903
363	0.026681	0.052906
373	0.026682	0.052908
383	0.026683	0.05291
393	0.026684	0.052912
403	0.026685	0.052915
413	0.026686	0.052917
423	0.026687	0.052918
433	0.026688	0.05292
443	0.026689	0.052922
453	0.026689	0.052924
463	0.02669	0.052925
473	0.026691	0.052927
483	0.026691	0.052928
493	0.026692	0.05293
503	0.026693	0.052931
513	0.026693	0.052932
523	0.026694	0.052933
533	0.026694	0.052935



Scheme 1. Reaction pathway for HDO of karanja oil over supported metal catalyst [27].

3.2 Reactions involved in HDO of karanja oil

The reactions involved in HDO of vegetable oil are in general quite complex in nature and depends strongly on types of catalyst used. For direct HDO of karanja oil, unsaturated triglycerides first undergone saturation in presence of hydrogen over supported metal catalyst (**Scheme 1**) [27]. Complete conversion of unsaturated triglycerides was considered in the present study. The saturated triglycerides were then transformed to corresponding fatty acids over supported metal catalyst with release of equivalent amount of propane. The fatty acids are then converted to hydrocarbons with one carbon less than fatty acid through dehydrogenation followed by decarbonylation of intermediate fatty alcohol [9]. The carbon monoxide formed in this reaction undergoes water gas shift reaction forming carbondioxide. The HDO of karanja oil predominately follow this route over supported metal catalysts. The conversion of triglycerides to hydrocarbon of one carbon less than fatty acid was thus considered as 90% for simplicity of analysis (**Eq.(iii)** of **Scheme 2**). A part of the fatty acids also converted to hydrocarbon of equal number of carbon atom as in fatty acid through dehydration followed by hydrogenation of intermediate fatty alcohol. The conversion of triglycerides to hydrocarbon of equal number of carbon atom as in fatty acid was deliberated as 5% (**Eq.(iv)** of **Scheme 2**). A small amount of cracking was also observed during HDO of karanja oil and overall conversion of triglycerides by cracking was considered as 5% (**Eq.(v-vi)** of **Scheme 2**). Over solid acids

supported metal catalysts, the HDO of vegetable oil however proceeds through combination of HDO, catalytic cracking, and hydroisomerization reactions. In UOP hydrorefining process, catalytic hydroisomerisation is carried out in a reactor for isomerising normal alkanes to branched paraffin rich diesel which improves the properties and meet the required specifications of diesel. The reaction can be controlled and it is more selective. It consumes very less hydrogen [10]. Generally, hydroisomerisation is practiced in petroleum industry with platinum as a catalyst which makes it more costly [28]. However, the hydroisomerization reactions were not considered in the present study due to unavailability of suitable information in open literature. In two-step HDO of karanja oil, the vegetable oil first undergoes hydrolysis thereby producing fatty acid and glycerol as shown in [Scheme 3](#). The fatty acids subsequently undergo HDO over supported metal catalyst as discussed before. The standard heat of reaction data reported in the [Scheme 2](#) and [Scheme 3](#) was obtained from Aspen Plus.

Reactions	ΔH_{298K}° , kJ/mole	Conversion, n, %	
Hydrogenation of triglyceride			
$C_{57}H_{104}O_6 + 3H_2 \rightarrow C_{57}H_{110}O_6$	-324.59	100	(i)
$C_{57}H_{98}O_6 + 6H_2 \rightarrow C_{57}H_{110}O_6$	-683.07	100	(ii)
Hydrodeoxygenation of triglyceride			
Decomposition of tristearin: $C_{57}H_{110}O_6 + 3H_2 \rightarrow C_3H_8 + 3C_{18}H_{36}O_2$			
Reduction of stearic acid: $3C_{18}H_{36}O_2 + 6H_2 \rightarrow 3C_{18}H_{38}O + 3H_2O$			
Dehydrogenation of fatty alcohol: $3C_{18}H_{38}O \rightarrow 3C_{18}H_{36}O + 3H_2$			
Decarbonylation of fatty alcohol: $3C_{18}H_{36}O \rightarrow 3C_{17}H_{36} + 3CO$	-458.04	90	(iii)
Water gas shift reaction: $3CO + 3H_2O \rightarrow 3CO_2 + 3H_2$			
<u>Overall: $C_{57}H_{110}O_6 + 3H_2 \rightarrow 3C_{17}H_{36} + C_3H_8 + 3CO_2$</u>			
Decomposition of tristearin: $C_{57}H_{110}O_6 + 3H_2 \rightarrow C_3H_8 + 3C_{18}H_{36}O_2$			
Reduction of stearic acid: $3C_{18}H_{36}O_2 + 6H_2 \rightarrow 3C_{18}H_{38}O + 3H_2O$			
Dehydration of fatty alcohol: $3C_{18}H_{38}O \rightarrow 3C_{18}H_{36} + 3H_2O$			
Hydrogenation of alkene: $3C_{18}H_{36} + 3H_2 \rightarrow 3C_{18}H_{38}$	-947.01	5	(iv)
<u>Overall: $C_{57}H_{110}O_6 + 12H_2 \rightarrow 3C_{18}H_{38} + C_3H_8 + 6H_2O$</u>			
Decomposition of tristearin: $C_{57}H_{110}O_6 + 3H_2 \rightarrow C_3H_8 + 3C_{18}H_{36}O_2$			
Reduction of stearic acid: $3C_{18}H_{36}O_2 + 6H_2 \rightarrow 3C_{18}H_{38}O + 3H_2O$			
Hydrocracking of fatty alcohol: $3C_{18}H_{38}O + 6H_2 \rightarrow 3C_{15}H_{32} + 3C_3H_8 + 3H_2O$	-1080.02	2.5	(v)
<u>Overall: $C_{57}H_{110}O_6 + 15H_2 \rightarrow 3C_{15}H_{32} + 4C_3H_8 + 6H_2O$</u>			
Decomposition of tristearin: $C_{57}H_{110}O_6 + 3H_2 \rightarrow C_3H_8 + 3C_{18}H_{36}O_2$			
Reduction of stearic acid: $3C_{18}H_{36}O_2 + 6H_2 \rightarrow 3C_{18}H_{38}O + 3H_2O$			
Hydrocracking of fatty alcohol: $3C_{18}H_{38}O + 6H_2 \rightarrow 3C_{16}H_{34} + 3C_2H_6 + 3H_2O$	-1070.69	2.5	(vi)
<u>Overall: $C_{57}H_{110}O_6 + 15H_2 \rightarrow 3C_{16}H_{34} + C_3H_8 + 3C_2H_6 + 6H_2O$</u>			

Scheme 2. Typical reactions during direct HDO of karanja oil.

Reactions	ΔH_{298K}° , kJ/mole	Conversi on, %	
Hydrolysis of tristearin			
$C_{57}H_{110}O_6 + 3H_2O \rightarrow C_3H_8O_3 + 3C_{18}H_{36}O_2$	-203	100	(i)
Hydrodeoxygenation of stearic acid			
Reduction of stearic acid: $C_{18}H_{36}O_2 + 2H_2 \rightarrow C_{18}H_{38}O + H_2O$			
Dehydrogenation of fatty alcohol: $C_{18}H_{38}O \rightarrow C_{18}H_{36}O + H_2$			
Decarbonylation of fatty alcohol: $C_{18}H_{36}O \rightarrow C_{17}H_{36} + CO$			
Water gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$	4.97	90	(ii)
<u>Overall: $C_{18}H_{36}O_2 \rightarrow C_{17}H_{36} + CO_2$</u>			
Reduction of stearic acid: $C_{18}H_{36}O_2 + 2H_2 \rightarrow C_{18}H_{38}O + H_2O$			
Dehydration of fatty alcohol: $C_{18}H_{38}O \rightarrow C_{18}H_{36} + H_2O$			
Hydrogenation of alkene: $C_{18}H_{36} + H_2 \rightarrow C_{18}H_{38}$	-164.34	5	(iii)
<u>Overall: $C_{18}H_{36}O_2 + 3H_2 \rightarrow C_{18}H_{38} + 2H_2O$</u>			
Reduction of stearic acid: $C_{18}H_{36}O_2 + 2H_2 \rightarrow C_{18}H_{38}O + H_2O$			
Hydrocracking of fatty alcohol: $C_{18}H_{38}O + 2H_2 \rightarrow C_{16}H_{34} + C_2H_6 + H_2O$			
<u>Overall: $C_{18}H_{36}O_2 + 4H_2 \rightarrow C_{16}H_{34} + C_2H_6 + 2H_2O$</u>	-205.34	2.5	(iv)
Reduction of stearic acid: $C_{18}H_{36}O_2 + 2H_2 \rightarrow C_{18}H_{38}O + H_2O$			
Hydrocracking of fatty alcohol: $C_{18}H_{38}O + 2H_2 \rightarrow C_{15}H_{32} + C_3H_8 + H_2O$			
<u>Overall: $C_{18}H_{36}O_2 + 4H_2 \rightarrow C_{15}H_{32} + C_3H_8 + 2H_2O$</u>	-208.88	2.5	(v)

Scheme 3. Typical reactions during two-step HDO of karanja oil.

Table 5. Summary of various equipment models used in the flowsheet with process conditions.

Direct HDO of karanja oil				Two-step HDO of karanja oil			
Reactor R1	RSTOIC model, (isothermal), 100 bar, H ₂ supplied/H ₂ consumed of 1.71, SRK property method.	573 K		Reactor R1	RSTOIC model, (isothermal), 56 bar, vegetable oil to water mass ratio of 2 (wt/wt), SRK property method.	533 K	
Reactor R2	RSTOIC model, (isothermal), 100 bar, H ₂ supplied/H ₂ consumed of 2, SRK property method.	623 K		Reactor R2	RSTOIC model, (isothermal), 100 bar, H ₂ supplied/H ₂ consumed of 1.5, SRK property method.	623 K	
Flash F1	FLASH3 model, 300 K, 100 bar, SRK property method.			Flash F1	FLASH3 model, 303 K, 56 bar, SRK property method.		
Flash F2	FLASH3 model, 300 K, 50 bar, CHAO-SEA property method.			Flash F2	FLASH3 model, 300 K, 100 bar, SRK property method.		
Compressor C1 and C3	MCOMPR model, two-stage isentropic compressor with inter-stage cooler with discharge pressure of 40 and 100 bar respectively.			Flash F3	FLASH3 model, 330 K, 60 bar, NRTL property method.		
Compressor C2	COMPR model, isentropic compressor with discharge pressure of 50 bar.			Distillation column DC1	RADFRAC model, 8 stages, no condenser, 2.3 reflux ratio, 1 st stage for feed, 10 bar condenser pressure, SRK property method.		
Distillation column DC	RADFRAC model, 10 stages, no condenser, kettle type reboiler, 1.3 reflux ratio, 1 st stage for feed, 20 bar condenser pressure, CHAO-SEA property method.			Distillation column DC2	RADFRAC model, 7 stages, 3 reflux ratio, 1 st stage for feed, 0.08 bar condenser pressure, NRTL property method.		
Heat exchanger HE1	HEATX model, counter current.			Compressor C1	MCOMPR model, two-stage isentropic compressor with inter-stage cooler with discharge pressure of 40 and 100 bar respectively.		
Heat exchanger HE2	HEATX model, counter current.			Compressor C2	COMPR model, isentropic compressor with discharge pressure of 40 bar.		
Pump P	PUMP model.			Pump P1-P3	PUMP model		
				Heat exchanger HE1 and HE2	HEATX model, counter current.		
				Evaporator E1	FLASH2 model, 323 K, 13.8 bar, NRTL property method:		
				Evaporator E2	FLASH2 model, 323 K, 8.27 bar NRTL property method:		

3.3 Process flow sheet

Conceptual process design for HDO of karanja oil for production of green diesel was developed using regressed property method and available equipment model in Aspen plus in model library. The details of two different processes (direct and two-step HDO of karanja oil) developed in the present work (Fig. 2) are outlined below.

3.3.1 Direct HDO of karanja oil

Fig. 3 shows the process flow sheet for direct HDO of karanja oil using Aspen plus. Due to unavailability of suitable kinetic model in open literature, RSTOIC reactor model was considered for HDO of karanja oil. However, RSTOIC reactor model cannot model simultaneous reactions in series. Therefore, HDO of karanja oil was subdivided into two reactors for simplicity of analysis. In the first reactor (R1), hydrogenation of unsaturated triglycerides took place; whereas HDO of saturated triglycerides took place in the second reactor (R2). The reaction stoichiometry and extent of reaction required for RSTOIC reactor model are outlined in Scheme 2. Based on literature survey, the conditions of the reactors were considered as 100 bar with temperature of 573 K and 623 K for R1 and R2 respectively. In this process, the preheated karanja oil at 573 K is pumped to the reactor R1. Hydrogen was compressed to 100 bar in two stages using a multi stage compressor model with alternative cooler and fed to the reactor R1. The H₂ supplied to reactor R1 was 1.71 times of stoichiometric requirement. The product from reactor R1 was then heated to 623 K and fed to reactor R2. The compressed H₂ was also sent to the reactor R2 that was 2.5wt% for 100wt% vegetable oil [29].

The products from the reactor R2 was cooled down to 300 K by vegetable oil feed stream using HeatX model before entering into flash column. The three-phase flash F1 operated under isothermal condition at 300 K was used to separate excess hydrogen (as top product) and water (as bottom product) from hydrocarbon product. 20% of hydrogen stream separated from F1 is purged and remaining is recycled after pressurizing it to 100 bar using compressor (C3). The hydrocarbon product from flash F1 is then sent to a distillation column (DC) to remove lighter hydrocarbons (C₂-C₃), carbon dioxide, and traces of hydrogen. DC was modelled using inbuilt RadFrac model in Aspen Plus which is a rigorous model for all types of multicomponent vapour-liquid fractionation. Number of stages, pressure and reflux ratio of the distillation column was optimized using sensitivity analysis in Aspen Plus for better separation of diesel range hydrocarbons from lighter hydrocarbons. Green diesel range hydrocarbon (C₁₃ to C₂₂)

was obtained from the bottom of the stripper. LPG range lighter hydrocarbons (C_2 and C_3) with traces of CO_2 was taken from the top of the stripper and sent to a three phase flash column F2 operated at 300K and 50 bar. The C_2 - C_3 separated from CO_2 and traces of hydrogen in flash F2 was sent to a splitter. A part of C_2 - C_3 stream was recycled to stripper as reflux for better fractionation. The various equipment and the conditions of operation used in the flowsheet are listed in [Table 5](#).

3.3.2. Two-step HDO of karanja oil

The process flowsheet for two-step HDO of karanja oil is shown in [Fig. 4](#). In this process, the triglycerides are decomposed to fatty acid and glycerol by water under high pressure. This is a quite commonly used industrial process (known as fat-splitting) especially in soap industries. In fat-splitting process, the triglycerides fed from the bottom reacts with water fed from the top producing fatty acids and glycerol[30][31]. The lighter fatty acids and heavier aqueous glycerol are withdrawn from the top and bottom of the fat-splitter respectively. However, due to unavailability of such kind of reactor model in Aspen Plus, combination of reactor (R1) and three-phase flash drum (F1) was used to represent fat-splitting section. Reactor was operated at 533 K and 56 bar and flash drum is operated at 3003 K and 56 bar.

The fatty acids stream from flash drum F1 was directed to reactor R2 that was operated at 623 K and 100 bar. Compressed hydrogen was fed to the reactor R2 where fatty acids were converted to hydrocarbons together with water and trace amount of C_2 - C_3 and CO_2 . However, due to unavailability of suitable kinetic model for these reactions in open literature, RSTOIC reactor model was used for both R1 and R2. The reaction stoichiometry and extent of reaction considered are shown in [Scheme 3](#) using tristearin as model triglyceride. The product stream (P2) was then cooled by a heat exchanger HE1 using karanja oil as cold stream. Cold product stream was then sent to three-phase flash tank F2 (operated at 300K and 100 bar) to separate gases (H_2 and CO_2) and water from hydrocarbon product.

The hydrocarbon product stream from flash F2 was sent to a distillation column (DC1) for separation of green diesel from lighter hydrocarbons (C_2 - C_3) and CO_2 . DC1 was RadFrac model with 8 stages and no condenser. Therefore, feed was fed from the 1st stage. Green diesel obtained as bottom product from DC1 was cooled in a heat exchange HE2 to pre-heat feed water for reactor R1. The lighter hydrocarbons (C_2 - C_3) and CO_2 separated as top-product from DC1 was passed into a flash tank to separate CO_2 from lighter hydrocarbons. A part lighter hydrocarbon stream was returned as reflux to the DC1. Reflux ratio on mole basis in DC1 was

6.2. The recovered lighter hydrocarbons could be considered as potential component for LPG. Since volume of this stream is quite small, this stream was not considered as co-product credit calculation in economic analysis.

Glycerine solution from F1 was fed to a double-effect evaporator where aqueous glycerol was concentrated from 18 wt% to 80 wt%. 80 wt% aqueous glycerol was further concentrated to 99 wt% using a vacuum distillation column DC2 (8kPa). The vacuum distillation column was designed using RadFrac model in Aspen Plus using NRTL as property method. The distillation column has 7 stages with 3rd stage as feed stage and reflux ratio of 3 on mole basis [32].

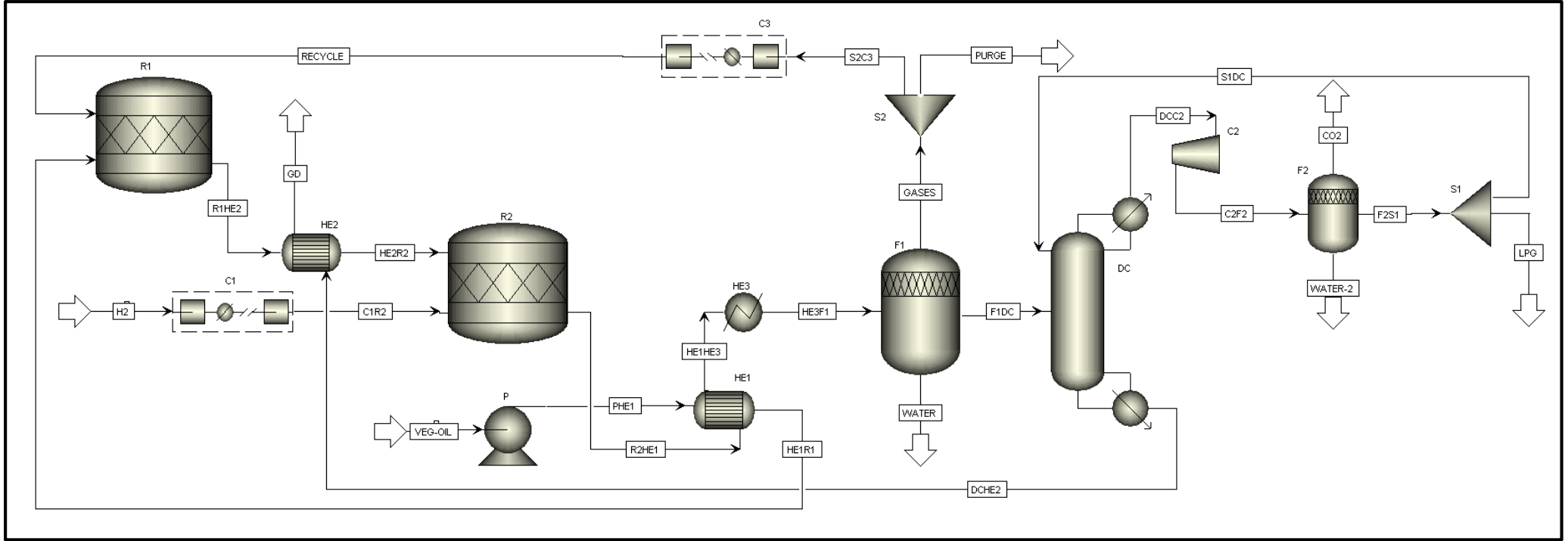


Fig. 3. Process flowsheet for direct hydrodeoxygenation of karanja oil using Aspen plus.

3.3.3. Economic analysis

The assumptions considered during economic analysis for calculation of capital and operating expenses are listed in Table 6. The analysis was performed considering 20 years of analysis with processing capacity of 0.12 million metric ton (MMT) karanja oil per annum. Straight line depreciation method is used to account depreciation of equipment with salvage value of 20% of initial capital investment. Volume of storage tanks was calculated considering feed storage of 12 days and product storage of 25 days [28]. Indirect cost includes interest on initial investment, depreciation, insurance and taxes. Interest rate is taken as 5.5% of total capital investment which is taken as 100% loan [33]. Considering all fixed and variable cost, operating expenses are calculated [34]. As liquefied petroleum gas (LPG) and glycerol are co-products for direct and two step HDO of karanja oil respectively. The revenue of selling these co-products was deducted from total production cost to obtain net total production cost. The production cost of green diesel expressed as \$/kg was then estimated based on net quantity of green diesel produced for different processing capacity. Estimates are assumed to be accurate to +/-25% of the actual project cost.

Table 6. Assumptions.

Capacity, million metric tons (MMT)	0.12
Karanja oil/annum	
Plant life, years	20 [18]
Operating hours, hours/year	8000
Number of working days, days/year	333
Depreciation method	Straight line
Working capital	5% of fixed capital investment
Operating charges	25% of operating labor cost
Plant overhead charges	50% of operating labor and maintenance cost
General and administration expenses	8% of direct cost (excluding rawmaterial cost)
Insurance and taxes	1.5% of total equipment cost [18]
Salvage value	20% of total equipment cost
Interest rate	5.5% of total capital investment [37]

The economics of the process was evaluated using Aspen Plus process economic analyser using default cost basis. The cost of various chemicals, raw materials, and utilities were obtained from literature as shown in Table 7. The cost of inedible karanja oil was however assumed to be 0.5 \$/kg based on local market survey. These data were incorporated in the process economic analyser. Economic evaluation in Aspen plus involves mapping all unit operations into individual equipment and calculating their size. However, in the present work, R-stoic reactor model was considered during process development. Therefore, size and cost of the reactor cannot be evaluated using Aspen Plus. Recent studies on HDO of vegetable oil showed complete conversion of vegetable oil to hydrocarbons in a fixed bed reactor at WHSV of 1.0 h⁻¹ [34]. The volume of fixed bed reactor was thus calculated considering WHSV of 1h⁻¹. The cost of HDO reactor was then calculated using six-tenth rule on the basis of naphtha hydrotreatment reactor since operating conditions are almost similar for both cases. The capital investment is highly sensitive to material of construction and hence desired material of construction information needs to be incorporated in Aspen Plus for accurate estimation of capital investment. Carbon steel is considered for the material of construction. On the basis of these information, economic analyser generates a report consisting of equipment summary, utilities, capital investment, operating cost, and cash flow [35]. Chemical costs are gathered from literature which is mentioned in Table 7. The capital investment and operating expenses are converted to year 2015 using chemical engineering plant cost index (CEPCI) [36]. Aspen economic analyser has given the economic report of the process for 2012 year which has been modified to 2015 using CEPCI.

Table 7. Cost of chemicals and utility.

Cooling water	0.12 \$/1000 gallons
Hydrogen	1.5 \$/kg [18]
Electricity	0.0775 \$/kWh [18][38]
Karanja oil	0.5 \$/kg
Water	0.09 \$/kg [30]
Propane	0.9534 \$/kg [37]
Glycerine	0.441 \$/kg [39]

4. RESULTS AND DISCUSSION

In the present work, the economics of two different processes was evaluated for several plant capacity in the range of 0.05-0.15 MMT karanja oil/annum to obtain an economically most attractive process for conversion of vegetable oil to green diesel. The overall material consumption and yield of various products with composition of the both process are reported in [Table 8](#) for a fixed processing capacity of 0.12 MMT of vegetable oil/annum. Hydrogen consumption is about 1283.11 MT/annum and 905.88 MT/annum for direct HDO process and two step HDO process respectively. Propane is produced from both the processes and 890.9 MT/annum of propane is more in the first process. By product glycerol is produced from two-step HDO process only because of hydrolysis of triglyceride. Green diesel produced from both the processes is nearly same which is about 74-75% of the karanja oil. In two-step HDO process, 60000 MT/annum of water is consumed for triglyceride hydrolysis process. 41918.9kWh and 23315.3 kWh of electricity needed for direct HDO and two step process respectively. Electricity consumption is more for the second process as compared to the first process. The detailed mass and energy balance for the flowsheet of [Fig. 3](#) and [Fig. 4](#) are obtained from Aspen Plus as reported in [Table 9](#) and [Table 10](#) respectively.

Table 8. Overall raw material and utility consumption and yield of various products for plant capacity of 0.12 MMT karanja oil/annum.

	Direct HDO	Two-step HDO
Hydrogen, MT/annum	1283.11	905.88
Propane, MT/annum	1094.2	203.3
Glycerol, MT/annum	-	10864.84
Green diesel, MT/annum	89070.12	89055.25
Electricity, kWh	41918.9	23315.3
Water, MT/annum	-	60000

The capital expenses included equipment cost, piping, civil, steel, instrumentation, electrical, insulation, paint, land, contingency and working capital, and other miscellaneous cost. Among which, equipment cost is the major contributing cost for investment. On the other hand, the operating expenses includes was subdivided into two parts: direct and indirect cost [28][34][37]. The direct cost includes operating labour and maintenance cost, utility cost, operating and plant overhead charge, raw material cost. The indirect cost includes depreciation,

interest, insurance and tax, and general and administration expenses. All cost data reported in the present work are expressed in US dollars in year 2015. The cost data acquired from literature for different year are re-estimated for year 2015 using Chemical Engineering Plant Cost Index (CEPCI) [36]. Based on these data, the unitary production cost of green diesel was evaluated. The details of economic analysis results are reported in [Table 11](#) and [Table 12](#) for direct and two step HDO of karanja oil respectively. As the capacity increases, production cost increases. For direct HDO of karanja oil, production cost of green diesel for 0.05, 0.10, 0.12, 0.15 MMT karanja oil/annum is 1.47, 1.27, 1.19, 1.17 \$/kg of green diesel respectively. Production cost of green diesel is less in the two step HDO process compared to the direct process as the by-product credit of glycerol has reduced the cost to less than a dollar. For this process, unitary production cost of green diesel for 0.05, 0.10, 0.12, 0.15 MMT karanja oil/annum was 1.03, 0.92, 0.9, 0.89 \$ respectively.

Table 9. Material and energy balance of direct HDO for plant capacity of 0.12 MMT karanja oil/annum.

	VEG-OIL	PHE1	HE1R1	RECYCLE	R1HE2	HE2R2	H2	C1R2	R2HE1	HE1HE3	HE3F1	WATER	GASES	PURGE
Temperature K	298.00	403.63	468.50	573.15	573.15	623.15	298.00	573.15	623.15	583.81	300.00	300.00	300.00	300.00
Pressure bar	1.00	100.00	100.00	100.00	100.00	100.00	1.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Total Flow kg/hr	13698.63	13698.63	13698.63	628.27	14247.71	14247.71	241.20	241.20	14489.16	14489.16	14489.16	140.91	785.34	157.07
Vapor Fraction	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00	0.62	0.60	0.35	0.00	1.00	1.00
Liquid Fraction	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.38	0.40	0.65	1.00	0.00	0.00
Enthalpy J/kg	2208700.00	1868200.00	1729100.00	6355800.00	1695500.00	1534400.00	2141.12	3982450.00	2356900.00	2488400.00	3261000.00	15833000.00	7157800.00	7157800.00
Entropy J/kg-K	-6005.43	-5578.03	-5260.45	-1473.16	-4326.72	-4057.31	47.11	-9483.75	-4490.10	-4707.83	-6486.40	-9011.60	-3367.03	-3367.03
Mass Flow kg/hr														
TRIPALMITIN	1547.95	1547.95	1547.95	0.00	1547.95	1547.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRISTEARIN	1150.68	1150.68	1150.68	0.00	10847.82	10847.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIOLEIN	7452.05	7452.05	7452.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIPALMITIN	506.85	506.85	506.85	0.00	506.85	506.85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRILINOLEIN	2164.38	2164.38	2164.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIBEHENIN	876.71	876.71	876.71	0.00	876.71	876.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C13H28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	26.51	26.51	26.51	0.00	0.00	0.00
C14H30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	28.53	28.53	28.53	0.00	0.00	0.00
C15H32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1293.54	1293.54	1293.54	0.00	0.00	0.00
C16H34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	271.79	271.79	271.79	0.00	0.00	0.00
C17H36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7909.98	7909.98	7909.98	0.00	0.00	0.00
C18H38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	474.44	474.44	474.44	0.00	0.00	0.00
C19H40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	393.31	393.31	393.31	0.00	0.00	0.00
C20H42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.55	39.55	39.55	0.00	0.00	0.00
C21H44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	662.43	662.43	662.43	0.00	0.00	0.00
C22H46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	38.54	38.54	38.54	0.00	0.00	0.00
WATER	0.00	0.00	0.00	0.43	0.00	0.00	0.00	0.00	166.81	166.81	166.81	140.57	0.54	0.11
CO2	0.00	0.00	0.00	484.03	401.34	401.34	0.00	0.00	2235.12	2235.12	2235.12	0.33	605.04	121.01
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2	0.00	0.00	0.00	80.65	0.01	0.01	241.20	241.20	115.22	115.22	115.22	0.00	100.82	20.16
C3H8	0.00	0.00	0.00	56.83	67.02	67.02	0.00	0.00	798.58	798.58	798.58	0.00	71.04	14.21
C2H6	0.00	0.00	0.00	6.32	0.00	0.00	0.00	0.00	34.80	34.80	34.80	0.00	7.90	1.58

Table 9. Material and energy balance of direct HDO for plant capacity of 0.12 MMT karanja oil/annum.

	S2C3	F1DC	S1DC	DCHE2	DCC2	C2HE4	HE4F2	WATER-2	CO2	F2S1	LPG	GD
Temperature K	300.00	300.00	300.00	698.14	299.99	366.78	300.00	300.00	300.00	300.00	300.00	638.33
Pressure bar	100.00	100.00	50.00	20.00	20.00	50.00	50.00	50.00	50.00	50.00	50.00	20.00
Total Flow kg/hr	628.27	13562.92	953.10	11144.91	3371.13	3371.13	3371.13	23.75	2155.93	1191.38	238.28	11144.91
Vapor Fraction	1.00	0.00	0.00	0.00	1.00	1.00	0.33	0.00	1.00	0.00	0.00	0.00
Liquid Fraction	0.00	1.00	1.00	1.00	0.00	0.00	0.67	1.00	0.00	1.00	1.00	1.00
Enthalpy J/kg	7157800.00	2904300.00	5492800.00	834810.00	6444600.00	6376300.00	6651300.00	16042000.00	7099000.00	-5492800.00	5492800.00	1040760.80
Entropy J/kg-K	-3367.03	-6654.74	-4973.68	-5012.59	-2782.50	-2739.95	-3586.67	-14200.34	-2471.44	-4973.68	-4973.68	-5324.87
Mass Flow kg/hr												
TRIPALMITIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRISTEARIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIOLEIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIPALMITIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRILINOLEIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIBEHENIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C13H28	0.00	26.51	0.00	26.51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	26.51
C14H30	0.00	28.53	0.00	28.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	28.53
C15H32	0.00	1293.54	0.01	1293.54	0.01	0.01	0.01	0.00	0.00	0.01	0.00	1293.54
C16H34	0.00	271.79	0.00	271.79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	271.79
C17H36	0.00	7909.98	0.01	7909.98	0.02	0.02	0.02	0.00	0.00	0.02	0.00	7909.98
C18H38	0.00	474.44	0.00	474.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	474.44
C19H40	0.00	393.31	0.00	393.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	393.31
C20H42	0.00	39.55	0.00	39.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.55
C21H44	0.00	662.43	0.00	662.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	662.43
C22H46	0.00	38.54	0.00	38.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	38.54
WATER	0.43	25.70	0.00	0.00	25.70	25.70	25.70	23.75	1.93	0.00	0.00	0.00
CO2	484.03	1629.76	404.86	0.00	2034.62	2034.62	2034.62	0.00	1528.75	506.07	101.21	0.00
CO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2	80.65	14.40	0.53	0.00	14.93	14.93	14.93	0.00	14.27	0.66	0.13	0.00
C3H8	56.83	727.54	537.33	6.29	1258.59	1258.59	1258.59	0.00	586.67	671.66	134.33	6.29
C2H6	6.32	26.91	10.36	0.00	37.27	37.27	37.27	0.00	24.32	12.95	2.59	0.00

Table 10. Material and energy balance of two-step HDO for plant capacity of 0.12 MMT karanja oil/annum.

	VEG-OIL	P1HE1	HE1R1	H2O	P2HE2	HE2R1	R1F1	FA	P3HE3	HE3R2	H2	C2HE5	R2HE1	HE1HE4
Temperature K	298.15	342.17	499.15	300.00	302.39	541.15	533.15	303.15	305.25	623.15	298.00	533.53	623.15	508.33
Pressure bar	1.00	55.00	55.00	1.00	55.00	55.00	56.00	56.00	100.00	100.00	1.00	80.00	100.00	100.00
Total Flow kg/hr	13698.63	13698.63	13698.63	6849.32	6849.32	6849.32	20548.21	13240.13	13240.13	13240.13	171.35	1881.27	13411.50	13411.50
Vapor Fraction	0.00	0.00	1.00	0.00	0.00	0.00	0.95	0.00	0.00	0.17	1.00	1.00	0.59	0.52
Liquid Fraction	1.00	1.00	0.00	1.00	1.00	1.00	0.05	1.00	1.00	0.83	0.00	0.00	0.41	0.48
Enthalpy J/kg	-2211485.7	-2025932.2	-1683004.4	-15857852.5	-15842939.1	-14796423.3	-5671899.8	-3002538.5	-2992114.6	-2151040.9	-1714.1	-8476725.1	-2340307.7	-2690577.5
Entropy J/kg-K	-6003.96	-5778.49	-4985.99	-9029.92	-8998.74	-6468.28	-4416.59	-6510.05	-6497.74	-4676.38	46.39	-440.33	-4594.06	-5202.42
Mass Flow kg/hr														
TRIPALMITIN	1547.95	1547.95	1547.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRISTEARIN	1150.69	1150.69	1150.69	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIOLEIN	7452.06	7452.06	7452.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIARACHIDIN	506.85	506.85	506.85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRILINOLEIN	2164.38	2164.38	2164.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIBEHENIN	876.71	876.71	876.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PALMITIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	1475.02	1475.02	1475.02	1475.02	0.00	0.00	0.00	0.00
STEARIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	1101.60	1101.60	1101.60	1101.60	0.00	0.00	0.00	0.00
LINOLINIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	2070.79	2070.79	2070.79	2070.79	0.00	0.00	0.00	0.00
OLEIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	7131.99	7131.99	7131.99	7131.99	0.00	0.00	0.00	0.00
ARACHIDIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	487.09	487.09	487.09	487.09	0.00	0.00	0.00	0.00
BEHENIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	845.23	845.23	845.23	845.23	0.00	0.00	0.00	0.00
C13H28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	26.51	26.51
C14H30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	28.53	28.53
C15H32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1293.54	1293.54
C16H34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	271.79	271.79
C17H36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7909.98	7909.98
C18H38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	474.44	474.44
C19H40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	393.31	393.31
C20H42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.55	39.55
C21H44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	662.43	662.43
C22H46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	38.54	38.54
WATER	0.00	0.00	0.00	6849.32	6849.32	6849.32	6015.26	126.32	126.32	126.32	0.00	8.35	293.13	293.13
CO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1793.21	1833.79	1833.79
H2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	171.35	0.01	58.02	58.02
C3H8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	46.76	51.04	51.04
C2H6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	32.92	34.80	34.80
GLYCEROL	0.00	0.00	0.00	0.00	0.00	0.00	1421.25	2.11	2.11	2.11	0.00	0.00	2.11	2.11

Table 10. Material and energy balance of two-step HDO for plant capacity of 0.12 MMT karanja oil/annum.

	HE4F2	GASES	WATER	F2DC1	SDC1	DC1HE2	GD	DC1C2	C2HE5	HE5F3	CO2	F3S	LPG
Temperature K	300.00	300.00	300.00	300.00	299.38	709.98	523.02	310.30	501.21	290.00	300.00	300.00	299.38
Pressure bar	100.00	100.00	100.00	100.00	60.00	10.00	10.00	10.00	60.00	80.00	60.00	60.00	60.00
Total Flow kg/hr	13411.50	67.95	324.39	13019.08	940.75	11143.05	11143.05	2767.10	2767.10	2767.10	1591.17	1175.94	235.19
Vapor Fraction	0.26	1.00	0.00	0.00	0.04	0.00	0.00	1.00	1.00	0.00	1.00	0.00	0.04
Liquid Fraction	0.74	0.00	1.00	1.00	0.96	1.00	1.00	0.00	0.00	1.00	0.00	1.00	0.96
Enthalpy J/kg	3254917.55	942505.62	15126071.04	2993607.10	8437323.80	772068.02	1415330.20	8545557.80	8367891.00	8835297.70	8746769.10	8437323.80	8437323.80
Entropy J/kg-K	-6565.94	-16201.48	-8191.87	-6579.27	-1750.88	-4958.57	-6001.74	-679.12	-554.08	-1912.92	-852.97	-1751.63	-1750.88
Mass Flow kg/hr													
TRIPALMITIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRISTEARIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIOLEIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIPALMITIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRILINOLEIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIBEHENIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PALMITIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STEARIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
LINOLINIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OLEIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ARACHIDIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BEHENIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C13H28	26.51	0.00	0.00	26.51	0.00	26.51	26.51	0.00	0.00	0.00	0.00	0.00	0.00
C14H30	28.53	0.00	0.00	28.53	0.00	28.53	28.53	0.00	0.00	0.00	0.00	0.00	0.00
C15H32	1293.54	0.00	0.00	1293.53	0.00	1293.53	1293.53	0.01	0.01	0.01	0.00	0.01	0.00
C16H34	271.79	0.00	0.00	271.79	0.00	271.79	271.79	0.00	0.00	0.00	0.00	0.00	0.00
C17H36	7909.98	0.00	0.00	7909.93	0.00	7909.93	7909.93	0.00	0.00	0.00	0.00	0.00	0.00
C18H38	474.44	0.00	0.00	474.44	0.00	474.44	474.44	0.00	0.00	0.00	0.00	0.00	0.00
C19H40	393.31	0.00	0.00	393.31	0.00	393.31	393.31	0.00	0.00	0.00	0.00	0.00	0.00
C20H42	39.55	0.00	0.00	39.55	0.00	39.55	39.55	0.00	0.00	0.00	0.00	0.00	0.00
C21H44	662.43	0.00	0.00	662.42	0.00	662.42	662.42	0.00	0.00	0.00	0.00	0.00	0.00
C22H46	38.54	0.00	0.00	38.54	0.00	38.54	38.54	0.00	0.00	0.00	0.00	0.00	0.00
WATER	293.13	0.19	289.79	3.14	10.26	0.01	0.01	12.83	12.83	12.83	0.01	12.82	2.56
CO2	1833.79	6.88	32.38	1794.51	828.73	0.84	0.84	2578.65	2578.65	2578.65	1542.73	1035.92	207.18
H2	58.02	58.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00
C3H8	51.04	1.11	0.04	49.89	79.91	3.61	3.61	121.98	121.98	121.98	22.10	99.88	19.98
C2H6	34.80	1.76	0.07	32.97	21.85	0.04	0.04	53.63	53.63	53.63	26.32	27.31	5.46
GLYCEROL	2.11	0.00	2.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 10. Material and energy balance of two-step HDO for plant capacity of 0.12 MMT karanja oil/annum.								
	GLY	W-1	E1E2	W-2	E2HE6	HE6DC2	W-3	GLYCEROL
Temperature K	303.15	323.15	323.15	323.15	323.15	473.15	315.29	481.15
Pressure bar	56.00	14.80	14.80	9.29	9.29	9.29	0.08	0.08
Total Flow kg/hr	7308.08	3774.25	3533.83	1766.06	1767.77	1767.77	408.31	1359.47
Vapor Fraction	0.00	1.00	0.00	1.00	0.00	0.56	0.00	0.00
Liquid Fraction	1.00	0.00	1.00	0.00	1.00	0.44	1.00	1.00
Enthalpy J/kg	14148302.52	13376038.88	12305570.42	13376034.69	8865821.14	8005442.12	14531235.62	-6804914.90
Entropy J/kg-K	-8416.84	-3549.28	-7637.90	-3334.12	-6720.55	-4861.45	-8395.22	-5498.25
Mass Flow kg/hr								
TRIPALMITIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRISTEARIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIOLEIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIPALMITIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRILINOLEIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TRIBEHENIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PALMITIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
STEARIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
LINOLINIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OLEIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ARACHIDIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BEHENIC ACID	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C13H28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C14H30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C15H32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C16H34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C17H36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C18H38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C19H40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C20H42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C21H44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C22H46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WATER	5888.94	3774.25	2114.69	1766.05	348.63	348.63	348.63	0.00
CO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C3H8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C2H6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GLYCEROL	1419.14	0.00	1419.14	0.00	1419.14	1419.14	59.67	1359.47

Table 11. Capital and operating expenses for direct HDO of karanja oil.

Plant capacity, MMT karanja oil/annum	Cost (\$)			
	0.05	0.10	0.12	0.15
Capital investment				
Equipment				
Storage tanks (2)	3070499	6096961	7362484	9211230
Compressor (3)	3230300	3292000	3405700	3510000
Reactors (2)	3085588	4642666	5173794	6050000
Flash vessels (2)	252800	263300	264600	298800
Distillation column (1)	355400	794800	406200	502300
Heat exchangers (4)	389800	454200	438100	529300
Pump (1)	96544	152861	160906	161000
Total equipment cost	10480930	15696788	17211784	20271587
Other investment				
Piping	590261	735205	660412	760132
Civil	892559	873045	890402	1017780
Steel	42464	57199	49734	54300
Instrumentation	1046540	1053150	1049980	1055930
Electrical	1273960	2006490	1853040	1964660
Insulation	136300	180136	162376	179110
Paint	21276	25525	24581	27173
Other	3572900	3833900	3743700	3842800
General and administrative overhead	903309	959676	937095	940636
Contract fee	762151	814460	795943	810581
Contingency	5735480	6093800	5950720	5975500
Total project capital cost	25545731	32407074	33447766	37000000
Land	510915	648141	668955	740000
Fixed capital investment	26102687	33147898	34173619	37834438
Working capital	1305134	1657395	1708681	1891722
Total capital investment	27407821	34805293	35882300	39726160
Production cost				
Direct cost				
Operating labour and maintenance cost	8031660	8132179	7971347	7740148
Utilities cost (steam, electricity, cooling water)	11917090	24026690	26182386	33373107
Karanja oil	25000000	50000000	60000000	75000000
Hydrogen	1500340	2089234	2605511	3676679
Operating charge	231199	231199	231199	231199
Plant overhead charge	4015830	4066090	3985673	3870074
Indirect cost				
Insurance and tax	157214	235452	258177	304074
Depreciation	838474	1255743	1376943	1621727
Interest	1507430	1914291	1973526	2184939
Other expenses				
General and administration expenses	1935662	2916493	3069648	3617162
Total operating cost	55134900	94867371	107654411	131619109
Co-product credit	625024	761589	1400176	1765522
Net production cost	54509875	94105781	106254235	129935740
Green diesel produced, kg/annum	37091571	74183188	89019774	111417178
Production cost of green diesel, \$/kg	1.47	1.27	1.19	1.17

Table 12. Capital and operating expenses for two-step HDO of karanja oil.

Plant capacity, MMT karanja oil/annum	Cost (\$)			
	0.05	0.10	0.12	0.15
Capital investment				
Equipment				
Storage tanks (4)	3020273	6440037	7737455	9676664
Compressor (2)	3087800	3340300	3385800	3385800
Reactors(2)	3085588	4642666	5173794	6052051
flash vessels (5)	574800	585900	577200	577200
Distillation column (2)	1007600	1355200	1551400	1551400
Heat Exchangers (6)	653200	733300	764800	764800
Pump (3)	266244	329461	339706	351606
Total Equipment Cost	11695504	17426865	19530155	22359522
Other investment				
Piping	947761	1134020	1203430	1478830
Civil	360936	483336	541056	635786
Steel	75363	84668	90937	97160
Instrumentation	1304590	1308410	1312340	1419650
Electrical	1038600	1305350	1423120	1723340
Insulation	264988	306939	328028	370921
Paint	35029	38112	38182	42561
Other	2088300	2311600	2409300	2824800
General and administrative overhead	422236	462793	479458	577375
Contract Fee	435839	478471	496063	581311
Contingency	2708460	2967520	3073800	3695010
Total project capital cost	21377606	28308084	30925869	35806265
Land	427552	566162	618517	716125
Fixed capital investment	21918850	29024796	31708859	36712818
Working capital	1095943	1451240	1585443	1835641
Total capital investment	23014793	30476036	33294302	38548459
Production cost				
Direct cost				
Operating labour and maintenance cost	2895016	2975432	2995537	3055850
Utilities cost (electricity, cooling water)	7340691	12657289	15175051	18919376
Karanja oil	25000000	50000000	60000000	75000000
Hydrogen	569695	1139390	1367269	1709086
Water	2054792	4109585	4931995	6164378
Operating charge	271408	271408	271408	271408
Plant overhead charge	1447508	1487716	1497769	1527925
Indirect cost				
Insurance and tax	175433	261403	292952	335393
Depreciation	935640	1394149	1562412	1788762
Interest	1265814	1676182	1831187	2120165
Other expenses				
General and administration expenses	1228427	1935463	2205089	2720000
Total operating cost	43122325	77783821	92024701	113424183
Co-product credit	4802962	9589046	11549287	14484473
Net production cost	38319363	68194775	80475414	98939710
Green diesel produced, kg/annum	37131963	74164374	89108071	111396209
Production cost of green diesel, \$/kg	1.03	0.92	0.90	0.89

4.1 Effect of plant capacity on unitary production cost

Plant capacity is the governing parameter deciding manufacturing cost. In general, manufacturing cost decreases with increasing plant capacity. In the present work, plant capacity was varied in the range of 0.05 to 0.15 MMT karanja oil/annum to obtain an optimum plant capacity. The unitary production cost of green diesel decreases with increasing plant capacity for both direct and two-step HDO of karanja oil as shown in Fig.5. This was due to disproportionate increase of fixed capital investment and proportional increase of operating cost with increasing plant capacity. The decrease of unitary production cost was quite sharp at relatively lower plant capacities. The cost difference however reduced gradually with increasing plant capacity. The decrease of unitary production cost was almost insignificant beyond 0.12 MMT karanja oil/annum for both direct and two-step HDO. Therefore, 0.12 MMT karanja oil/annum was considered as the optimum plant capacity. Hence, all subsequent analysis was performed using 0.12 MMT karanja oil/annum as base case. At the optimum plant capacity, the unitary production cost was 1.282 \$/kg and 0.918 \$/kg of green diesel for direct and two-step HDO respectively.

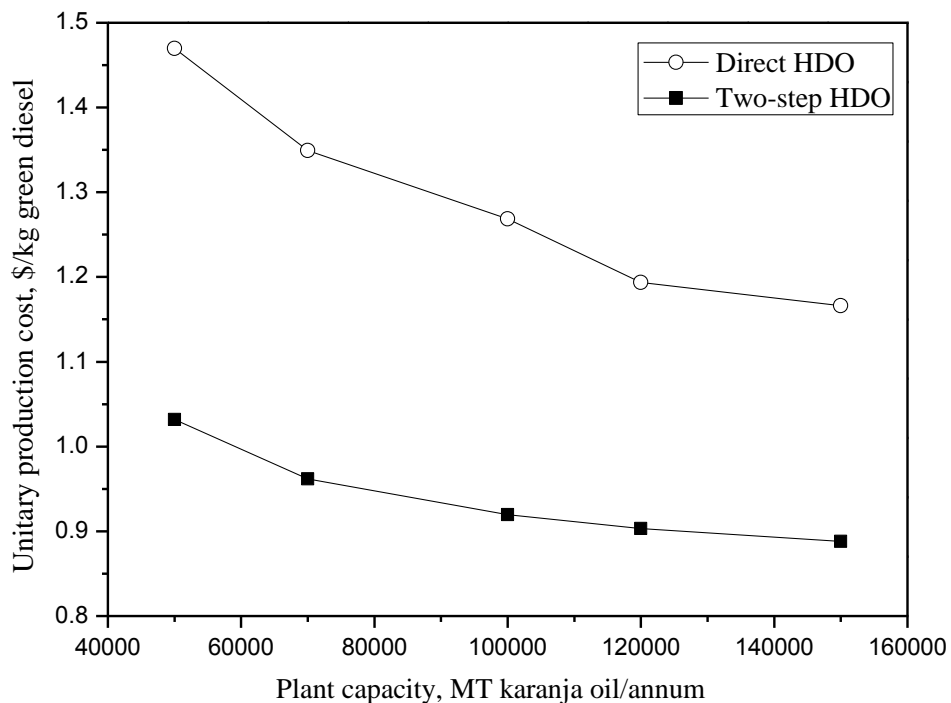


Fig. 5. Effect of plant capacity on unitary production cost of green diesel.

4.2 Effect of karanja oil cost on unitary production cost

The cost of vegetable oil is highly sensitive depending on types, geographical location, and year of consideration. On the other hand, cost of feedstock contributes significantly to the overall manufacturing cost. Therefore, effect on unitary production cost of green diesel was analyzed as shown in Fig. 6. As observed from the figure, the unitary production cost of green diesel increased linearly with the cost of karanja oil. It was observed that 10% increase of feedstock cost resulted about 5% increase of unitary production cost of green diesel.

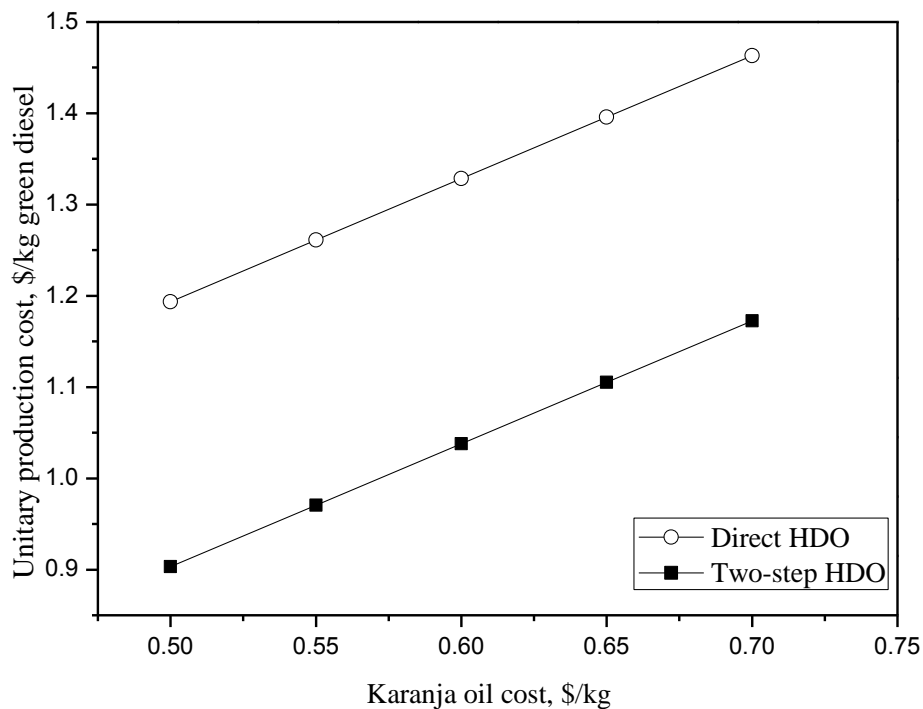


Fig. 6. Effect of karanja oil cost on unitary production cost of green diesel.

4.3 Contribution of various factors on unitary production cost

The analysis of contribution of parameters to the manufacturing cost is extremely important to identify most significant cost contributing parameter for possible reduction of manufacturing cost in near future. Share of various cost contributing factors to unitary production cost of green diesel for various plant capacity are shown in Fig. 7 and Fig. 8 for direct and two-step HDO of karanja oil respectively. As observed from the figure, with increasing plant capacity, the contribution of raw materials towards unitary production cost increased with simultaneous decrease of contribution of general and administrative expenses, indirect cost, plant overhead

and operating charges, and operating labor and maintenance. The feedstock (karanja oil) was the most cost contributing factor followed by utility in the process of conversion of karanja oil to green diesel. For 0.12 MMT karanja oil/annum plant capacity, the karanja oil alone contributed about 57% and 73% of unitary production cost of green diesel for direct and two-step HDO process respectively. It was also reported that feedstock cost accounts 70-80% of the total production cost of biodiesel [38]. The hydrogen is an expensive chemical required for HDO of triglycerides. The hydrogen accounted about 3-4% of the unitary production cost. On the other hand, utility accounts for about 20% of unitary production cost. Therefore, availability of inexpensive sources of triglycerides is extremely important to make the process economically attractive in near future. Propane and glycerol were the co-product for direct and two-step HDO of karanja oil respectively. These co-products can be sold to generate revenue for the process. The glycerol generated about 14% revenue for two-step HDO process compared to only about 1% by propane for direct HDO of karanja oil.

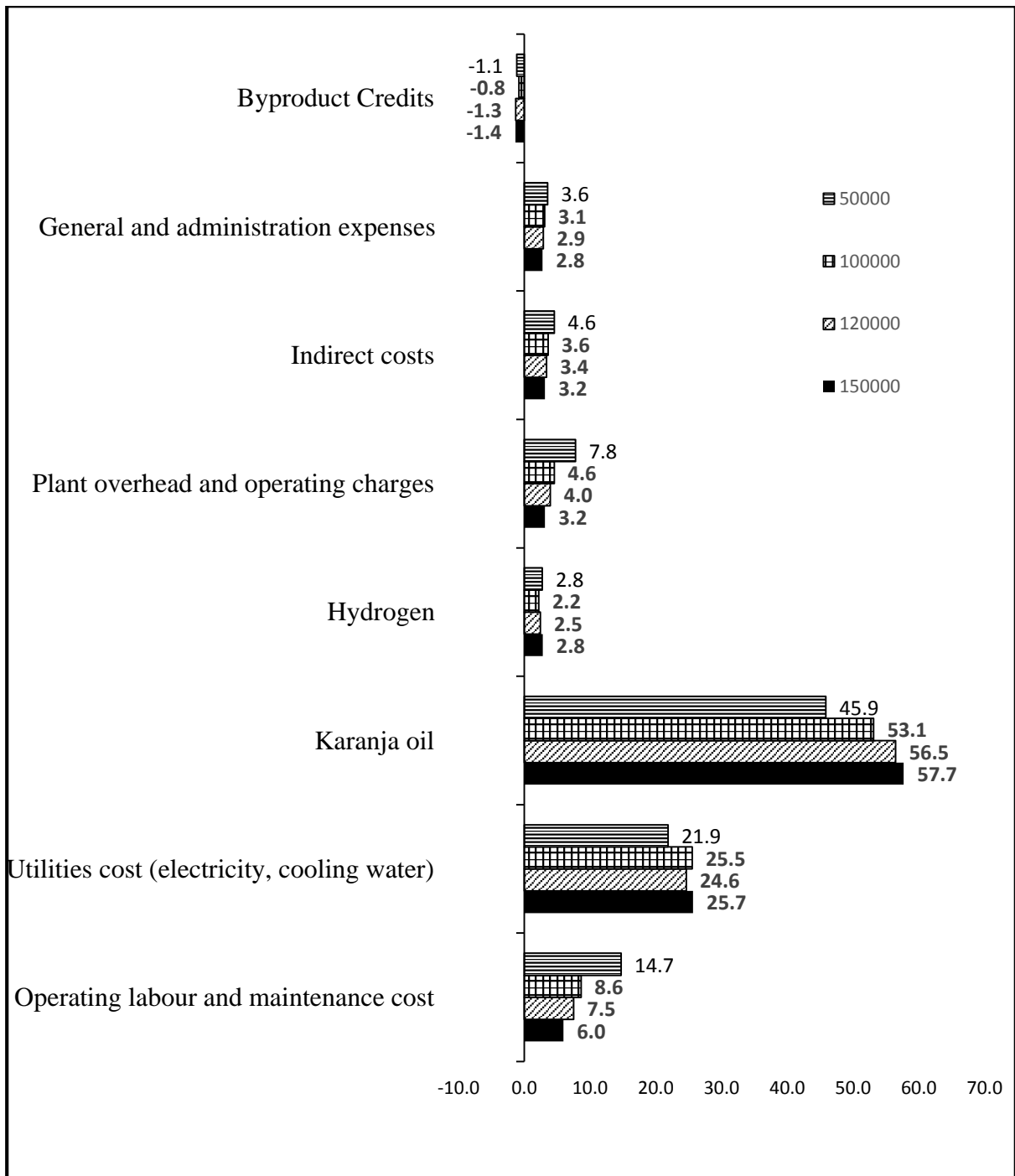


Fig. 7. Contribution of various factors to the unitary production cost of green diesel for direct HDO of karanja oil.

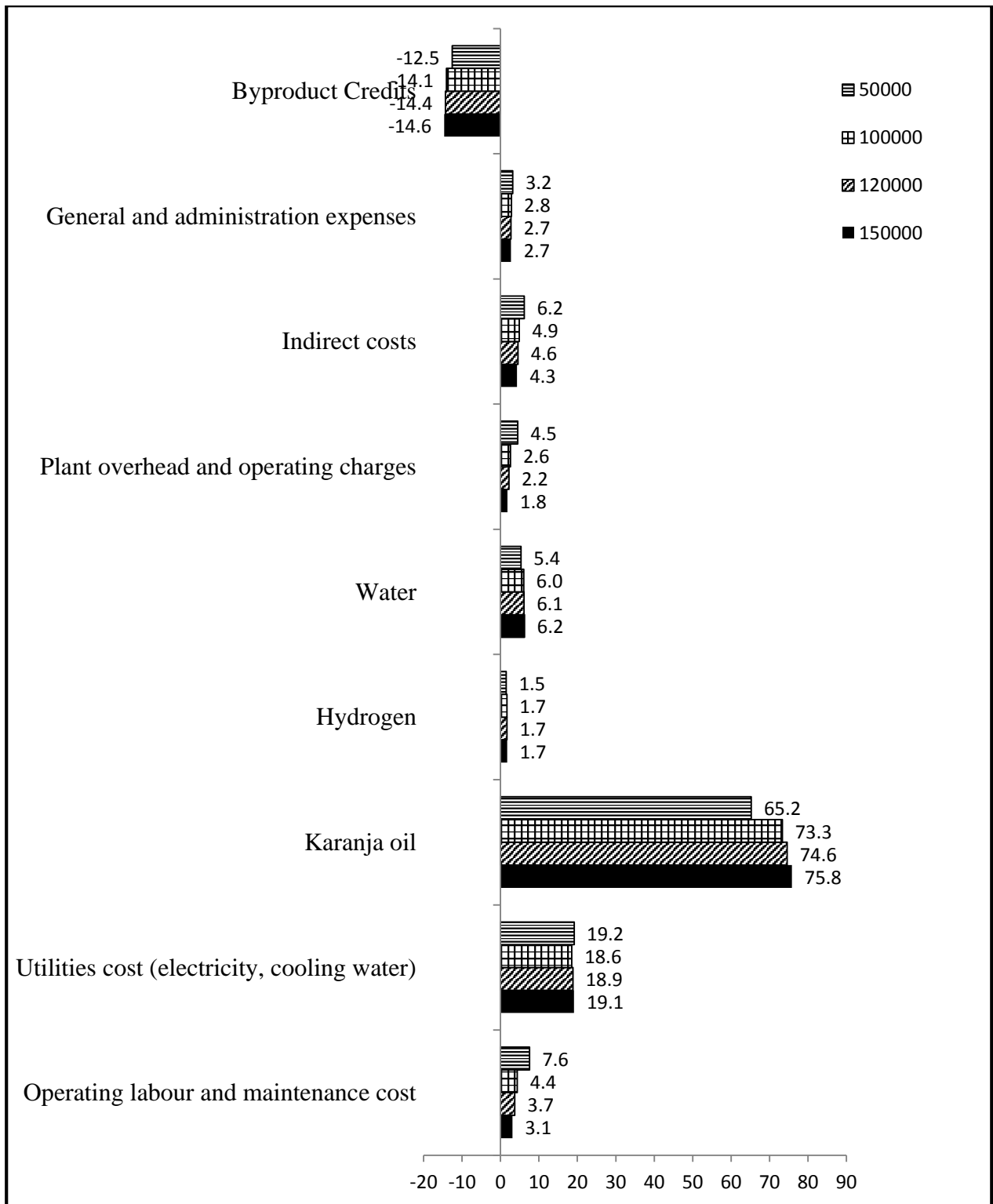


Fig. 8. Contribution of various factors to the unitary production cost of green diesel for two-step HDO of karanja oil.

Tao and Aden reported production cost of \$2.55/gallon biodiesel from soyabean oil in 2007 (equivalent to \$2.8135/gal in 2015 based on CPECI) for plant capacity of 45 MM gal biodiesel/year [18]. Economic analysis on production of green diesel from autotrophic

microalgae showed production cost of \$9.84/gal of diesel and \$20.53/gal of diesel via open raceway pond and photo-bioreactor respectively [19]. In the present work, unitary production cost of green diesel from karanja oil was found to be 3.537 \$/gal and 2.709 \$/gal of green diesel through direct and two-step process respectively for plant capacity of 40 MM gal of green diesel/year considering 0.5 \$/kg as cost of karanja oil. Diesel retail price was 3.83 \$/gallon in 2014 based on statistical data reported by US Energy Information Administration [39]. The cost of green diesel produced by HDO of karanja oil is thus quite competitive with retail price of petro-diesel. On the other hand, physicochemical properties of green diesel are comparable to petro-diesel allowing direct application in internal combustion engine. Therefore, it is quite expected that HDO of vegetable oil is going to be a dominating technology in near future.

5. CONCLUSION

The present work delineates a novel approach to conceptual processes design and economic feasibility analysis of direct and two-step HDO of karanja oil using Aspen Plus. HDO of inedible karanja oil produces fully renewable green diesel suitable for direct application in existing internal combustion engine. The unitary production cost of green diesel was then estimated for both direct and two-step HDO of karanja oil based on total capital investment and operating cost for several plant capacities. The unitary production cost of green diesel decreased significantly with increasing plant capacity with 0.12 MMT karanja oil/annum being observed as optimum capacity. For 0.12 MMT karanja oil/annum plant capacity, the unitary production cost was 1.198 \$/kg and 0.9181 \$/kg of green diesel in the year 2015 for direct and two-step HDO respectively. Co-product glycerol produced during two-step HDO of karanja oil generated huge revenue accounting about 14% of unitary production cost compared to only about 2% for co-product propane for two-step HDO. The feedstock (karanja oil) has significant impact on the overall production cost contributing about 57% and 73% of unitary production cost of green diesel for direct and two-step HDO process respectively. On the other hand, share of expensive hydrogen on overall manufacturing cost was only about 2%. Inexpensive feedstock and improvement of processing technology is expected to improve the overall economics of whole process further. Analysis further revealed that cost of green diesel is economically competitive to biodiesel and current petro-diesel. HDO of triglycerides has thus huge potential for upcoming technological development.

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