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ANALYSIS OF PETROLEUM PRODUCTION FROM COCONUT HUSKS AND SHELLSBY FISCHER–TROPSCH PROCESS

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Abstract*-Fischer–Tropsch process (F-T) is an efficient technology to synthesize clean and carbon-neutral liquid transportation fuel. In this paper, a process flow diagram of the incorporated system was generated and process simulation was carried out using Aspen HYSYS 2006 to model Fischer-Tropsch process using coconut husk and shell for producing propane and n-hexane as the principal products. Furthermore, economic analysis was performed for profit maximization by cost optimizing. The results of this simulation showed that 400 kg-mole/h of biomass from coconut husks and shells produced 15.21 kg-mole/h of petroleum products giving maximum annual profit of $ 64.56 million for the production of approximately 99% pure propane and 99% pure hexane. The results suggested that the process have a bright prospect economically. Thus, along with satisfying the social and environmental concerns, it could gradually substitute a significant share of the fossil fuels requirement to meet the rising global energy demand.*

Keywords: Coconut husks and shells, Fischer-Tropsch process, Syngas, HYSYS simulation and cost optimization.

1. INTRODUCTION

A huge share of the world's energy demands is being met by traditional fossil fuels, such as petroleum and natural gas. Liquid hydrocarbon is found to be the most attractive and feasible form of transportation fuel due to its favourable energy density and stability properties. Rise in global energy requirement and greenhouse gas emissions necessitate the utilisation of renewable sources of energy. Because of its versatility, availability and renewability, biomass can serve as a universal source of energy [1,2]. In the present situation of energy crisis, the use of coconut as energy source is a promising option as it is a permanent crop and non-seasonal. Although there has been much interest in the potential use of coconut oil as diesel fuel substitute, only 10% of the weight of the nut is coconut oil. An order of magnitude of 38.5 million liters of gasoline equivalent/year on 10,500 liters gasoline equivalent per day can be obtained from only 1% of the shells [3].

Fischer–Tropsch synthesis is a set of catalytic processes that can be used to produce fuels from synthesis gas derived from natural gas, coal, or biomass. During this process, CO is adsorbed on the surface of a transition metal (Co, Ni, and Fe) and hydrogenated producing CH_x monomers which consequently propagate to produce hydrocarbons [4].

Biomass such as coconut coir and shells, woodchips, straw stalks are first pre-treated by drying and pyrolysis before gasification. Then a cleaning process is applied to remove impurities to produce clean bio-syngas which meets the Fischer–Tropsch synthesis requirements. The syngas thus obtained is then conducted into a Fischer–Tropsch catalytic reactor to produce green gasoline, diesel and other clean biofuels [5].

In this project, the simulation and optimization of combustible gas production from coconut shell and husk using gasification technique and the conversion of the produced syngas to fuel by the Fischer-Tropsch process have been studied using Aspen HYSYS 2006. Fischer–Tropsch synthesis is gaining increasing interest because of its ability to produce environmentally friendly clean fuels containing little or no sulfur [6]. However, the major hindrence to the use FTS is the economic feasibilty. This paper studies the potential production costs and profit gain, and hence identifies the optimum process configurations and successful development pathways. The simulation can be thus used for scale-up and design of a commercial FTS plant [7].

2. PROCESS DESCRIPTION

There are mainly three steps in the biomass to liquid via Fischer–Tropsch synthesis. Biomass is firstly converted into biomass-derived syngas by gasification.

The impurities present in the raw syngas can lessen the FT activity in the catalytic conversion. Hence inthe second step syngas is cleaned. Finally an F-T reactor, with a metal-based catalyst, is used to convert the syngas to a mixture of hydrocarbons.

2.1 Gasification

The key to gasifier design is to create conditions such that biomass is reduced to charcoal which is later converted at suitable temperature to produce CO and H_2.In a gasifier, four distinct processes take place. They are: i) Drying of biomassii) Pyrolysisiii) Combustioniv) Reduction.

Dried biomass gives more efficient gasification, but drying reduces hydrogen content in the gas product. Pyrolysis involves direct thermal decomposition of biomass in the absence of oxygen at a reasonable temperature of around 400°C to 800°C [5,8]. The biomass, thus pre-treated, undergoes a series of oxidation and reduction reactions to produce the syngas. By the extensive use of the HYSYS's reaction manager, the production of syngas was modelled using four different conversion reactions grouped into two reaction sets that were used in two different reactors, viz, the combustor and the reactor.

(a) Combustor: Coconut husk and shell was the source of carbon and hydrogen, which were burnt in the combustor. Preheated air mixed with a recycle stream entered the combustor at a controlled flow rate. The oxygen was consumed in an exothermic combustion reaction generating a theoretical oxidation temperature of 1450°C.

(b) Reduction tower: The products of combustion were then passed through a red-hot charcoal bed where reduction takes place.

The reactors used for the gasification process are very similar to those used in combustion processes. The most widely used types are updraft and downdraft gasifiers which are fixed bed in nature. They are relatively easy to design and operate, and are therefore useful [9,10]. Again, bubbling and circulating fluidized bed gasifiers are also advantageous because of extremely good mixing and high heat transfer, resulting in very uniform bed conditions and efficient reactions [11]. The choice and design of gasifiers depends on operating conditions and different oxidants used for gasification. The simplest way of gasifying solid fuels is air gasification which results in a nitrogen-rich fuel gas. Gasification with pure oxygen is costly but results in a higher quality mixture of carbon monoxide and hydrogen and virtually no nitrogen. Steam gasification involves using steam as oxidants and is more commonly called "reforming". Other alternatives are a mixture of air/oxygen and oxygen rich air and/or steam [5]. In this simulation, air gasification method was used for biomass oxidation.

2.2 Gas cleaning

Gas cleaning includes removal of particulate matter and traces contaminants such as sulfur, oxygen, ammonia, dust and soot. Sulfur, being extremely active catalyst poison, can limit the catalytic process and result in high expenses for catalyst replacement [12]. Sulfur sorbent like ZnO can be used to absorb H_2S to protect catalysts. Oxygen present in the raw syngas may cause severe explosion during the compression before FT reaction. O_2 content can be reduced to below 0.5 vol% by deoxidizers packed with Pd/Al_2O_3 based de-oxidant or membrane separation. If biomass contains nitrogen, it will form NH_3 and NO_x in the gasification step. Ammonia can be removed by aqueous scrubber, or can be decomposed and selectively oxidized. NO_xcan be removed over the platinum and metals (Cu, Cr and Fe) based on zeolite catalysts. By using cyclones, metal filters, moving beds and bag filters, dust, soot and other impurities can be removed effectively [5].

In this paper, coconut husk and shell was assumed to be composed of C, H and O only and their composition is shown in table 1. Therefore, removal of sulfur and nitrogen compounds from the raw syngas was not required. The synthesis gas was separated from carbon dioxide and excess oxygen using three separators.

Table 1: Composition of coconut husk and shell

Element	C	H	O
Weight %	48.1	5.8	46.1

2.2 Fischer Tropsch reaction

Commercially established FT reactors can be divided into three main categories: fixed bed, fluid bed and slurry FT reactors. These reactors have two different temperature ranges depending on the types and quantities of desired Fischer-Tropsch products. The high temperature FT (HTFT) reactor runs with iron catalysts at around 340°C, and is used to produce olefins and gasoline. The low temperature FT (LTFT) reactor uses iron or cobalt based catalysts at around 230°C, and is used to produce diesel and linear waxes [5]. Additional processing such as distillation of the F-T products yields pure gasoline [12]. In this simulation, HTFT reactor with iron catalyst was considered to produce propane and n-hexane. The conditions used in this simulation in the Fischer-Tropsch reactor are summarized below:

Temperature: 340°C
Pressure: 25 bar
Catalyst: iron

3. CHEMICAL REACTIONS

The major reactions of this simulation take place in the combustion and reduction zones and in the Fischer-Tropsch reactor.

(a) Combustion zone: The combustible substance of a solid fuel is usually composed of carbon, hydrogen and oxygen. In complete combustion, carbon dioxide is obtained from carbon in fuel and water is obtained from the hydrogen, usually as steam. The following exothermic reactions occur in the combustion zone:

$$C + O_2 = CO_2 \ (\Delta H = -393 \text{ MJ/kg mole})$$

$$2H_2 + O_2 = 2H_2O \ (\Delta H = -242 \text{ MJ/kg mole})$$

(b) Reduction zone: The products of partial combustion (water, carbon dioxide and non-combustible partially cracked pyrolysis products) then pass through a red-hot charcoal bed where the following reduction reactions take place:

$$C + CO_2 = 2CO \; (\Delta H = -164.9 \text{ MJ/kg mole})$$

$$C + H_2O = CO + H_2 \; (\Delta H = -122.6 \text{ MJ/kg mole})$$

(c) Fischer-Tropsch reactor: The primary Fischer-Tropsch reactions are represented in the following equations [13]:

$$nCO + (2n+1)\, H_2O = C_nH_{(2n+2)} + nH_2O$$

The reactions for propane and hexane production are:

$$3CO+7H_2= C_3H_8+3H_2O$$

$$6CO+13H_2=C_6H_{14}+6H_2O$$

4. PROFIT OPTIMIZATION

Optimization means finding an alternative with the most cost effective or highest achievable performanceunder the given constraints, by maximizing desired factors and minimizing undesired ones.

4.1 Importance of optimization

For any production plant like production of petroleum by Fisher-Tropsch process, optimization study is performed in order to find optimum parameters for maximum production. The minimum energy required and optimum operating conditions of FT process can be determined through the changes of system variables, such as temperature, H_2/CO ratio, reflux ratio of distillation column, purity of products etc.

4.2 Assumptions for optimization

The simulation procedures were carried out to determine optimum condition of process by varying compositions of the products propane and n-hexane, operating temperature of alkane which was fed to the distillation column, temperature of the heated air and molar flow rate of mixed air to the combustor.

During the simulation, several considerations were made for optimization.Cost of oxygen fed to the combustor was neglected since atmospheric air was used as the source. Cost of coconut husk was considered \$150/ton (\$0.165/kg) [14] and cost of heating and cooling was assumed to be equivalent to the cost of electrical energy consumed (\$0.12/kWh) [15]. Selling prices of propane and n-Hexane were considered to be \$845.34/m^3[16] and \$8794.42/m^{3}respectively [17].

4.3 Equations and units used for optimization

In this simulation, the total profit was calculated by equation (1).

$$P = (845.34 \times V_P + 8794.42 \times V_H) - (0.165 \times M_f + 0.12 \times \sum Q_i) \qquad (1)$$

Here, P denotes profit in dollars (\$), V_P and V_H are the actual volumetric flow rates of propane and n-hexane respectively in m^3/h, M_f is mass flow rate of coconut husk and shell in kg/h and Q_i denotes total amount of heating and cooling duty in kilowatt.

5. RESULTS AND DISCUSSIONS

5.1 Results from simulation

The process flow diagram (PFD) simulated in Aspen HYSYS 2006 is shown in Fig. 1. The properties of different streams of this process are summarized in Fig. 2.From the worksheet, it was obtained that 9.932kg-mole/h of propane and 5.276kg-mole/h of n-Hexane can be produced from 400 kg-mole/h coconut husks and shells.

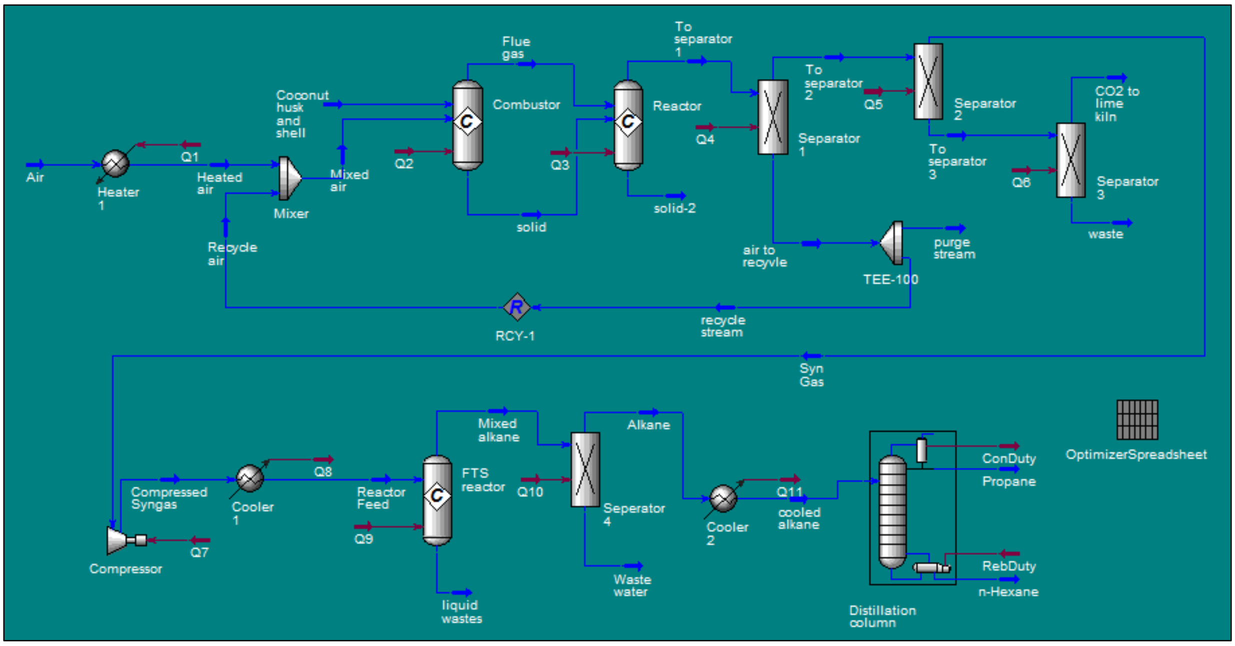
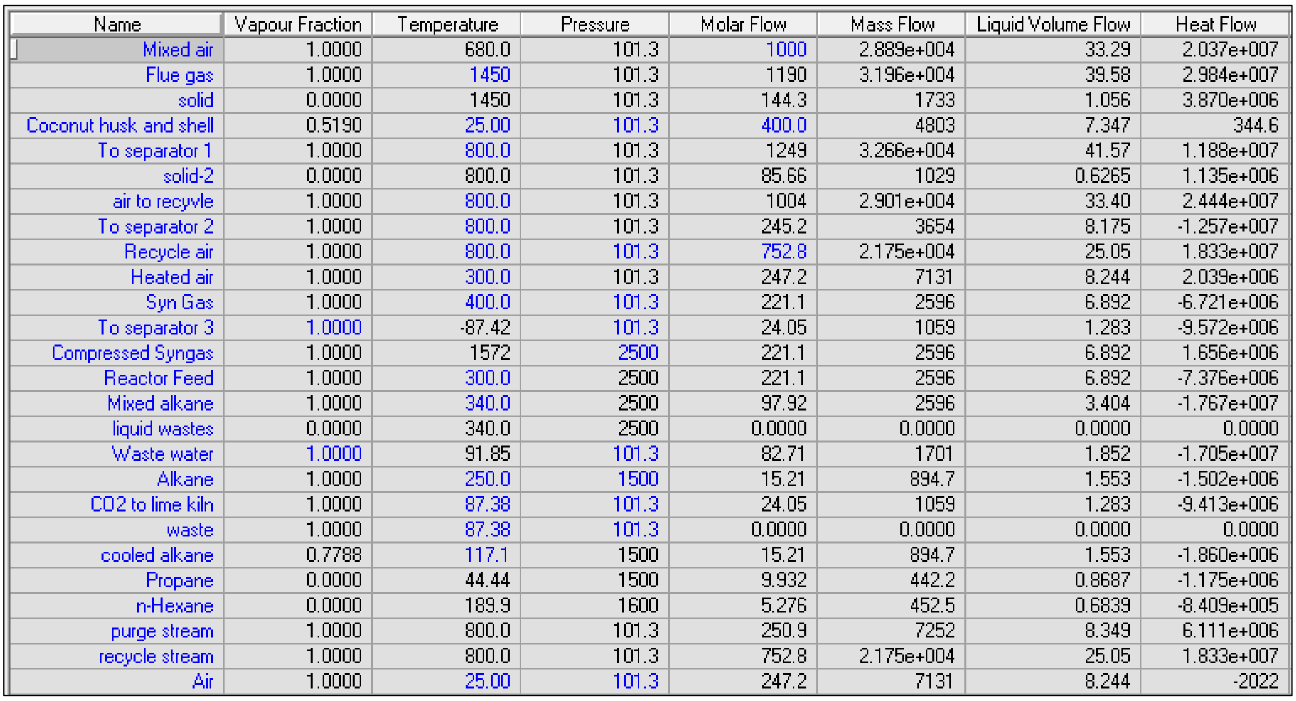


Fig.1: Process flow diagram of petroleum production from coconut husk and shell.



Name	Vapour Fraction	Temperature	Pressure	Molar Flow	Mass Flow	Liquid Volume Flow	Heat Flow
Mixed air	1.0000	680.0	101.3	1000	2.889e+004	33.29	2.037e+007
Flue gas	1.0000	1450	101.3	1190	3.196e+004	39.58	2.984e+007
solid	0.0000	1450	101.3	144.3	1733	1.056	3.870e+006
Coconut husk and shell	0.5190	25.00	101.3	400.0	4803	7.347	344.6
To separator 1	1.0000	800.0	101.3	1249	3.266e+004	41.57	1.188e+007
solid-2	0.0000	800.0	101.3	85.66	1029	0.6265	1.135e+006
air to recyvle	1.0000	800.0	101.3	1004	2.901e+004	33.40	2.444e+007
To separator 2	1.0000	800.0	101.3	245.2	3654	8.175	-1.257e+007
Recycle air	1.0000	800.0	101.3	752.8	2.175e+004	25.05	1.833e+007
Heated air	1.0000	300.0	101.3	247.2	7131	8.244	2.039e+006
Syn Gas	1.0000	400.0	101.3	221.1	2596	6.892	-6.721e+006
To separator 3	1.0000	-87.42	101.3	24.05	1059	1.283	-9.572e+006
Compressed Syngas	1.0000	1572	2500	221.1	2596	6.892	1.656e+006
Reactor Feed	1.0000	300.0	2500	221.1	2596	6.892	-7.376e+006
Mixed alkane	1.0000	340.0	2500	97.92	2596	3.404	-1.767e+007
liquid wastes	0.0000	340.0	2500	0.0000	0.0000	0.0000	0.0000
Waste water	1.0000	91.85	101.3	82.71	1701	1.852	-1.705e+007
Alkane	1.0000	250.0	1500	15.21	894.7	1.553	-1.502e+006
CO2 to lime kiln	1.0000	87.38	101.3	24.05	1059	1.283	-9.413e+006
waste	1.0000	87.38	101.3	0.0000	0.0000	0.0000	0.0000
cooled alkane	0.7788	117.1	1500	15.21	894.7	1.553	-1.860e+006
Propane	0.0000	44.44	1500	9.932	442.2	0.8687	-1.175e+006
n-Hexane	0.0000	189.9	1600	5.276	452.5	0.6839	-8.409e+005
purge stream	1.0000	800.0	101.3	250.9	7252	8.349	6.111e+006
recycle stream	1.0000	800.0	101.3	752.8	2.175e+004	25.05	1.833e+007
Air	1.0000	25.00	101.3	247.2	7131	8.244	-2022

Fig.2: Properties of different streams of the process simulated in Aspen HYSYS 2006

5.2 Graphical representations

The effect of different process variables on the production of propane and n-hexane were studied and a number of graphs were generated for this purpose. These graphs give the relations among respective process variables and are essential implement for design of FT reactor as well as distillation column for commercial purpose.

(a)Effect of distillation column feed temperature on propane production: It was apparent from Fig. 3 that the separation of propane was insignificant up to a temperature (approximately 120°C). After this temperature, molar flow of propane increased almost linearly with increasing temperature.

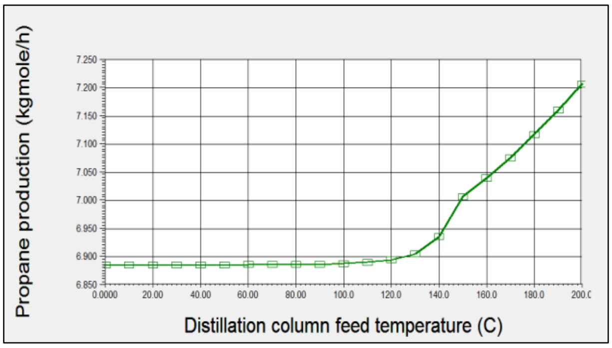


Fig.3: Effect temperature on propane production

(b)Effect of distillation column feed temperature on n-hexane production: Figure 4 showed the opposite effect of temperature on molar flow of hexane. Below a certain temperature (approximately 120°C) the flow rate of hexane was quite significant and production per hour was almost constant.But it gradually decreased with increasing temperature after 120°C.

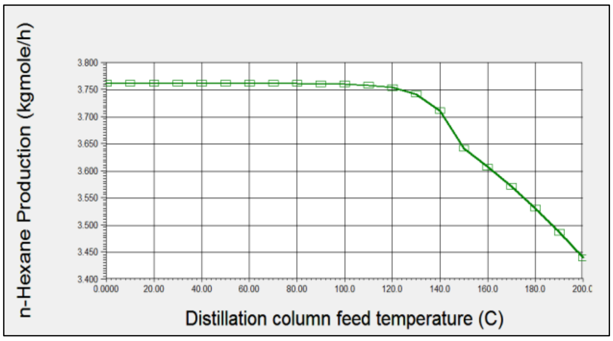


Fig.4: Effect of temperature on n-hexane production

(c) Effect of synthesis gas pressure on heat flow (Q9): Figure 5 affirmed that higher the pressure of synthesis gas, lesser the energy required for the reaction in the FT reactor.

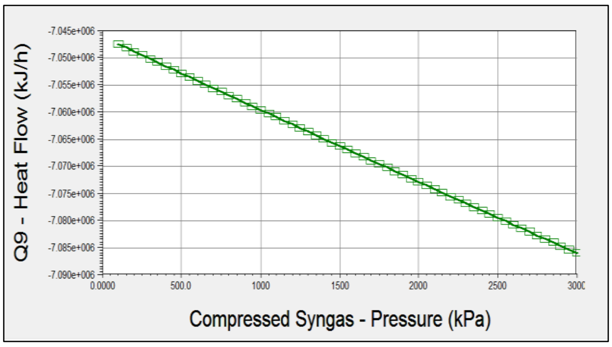


Fig. 5: Effect of synthesis gas pressure on heat flow (Q7)

(d) Effect of coconut shell and husk temperature on combustor heat flow (Q2): Figure 6illustratedthe fact that less energy would be required in the gasifier if the coconut husk and shells were heated to a higher temperature prior to entry to the gasifier.

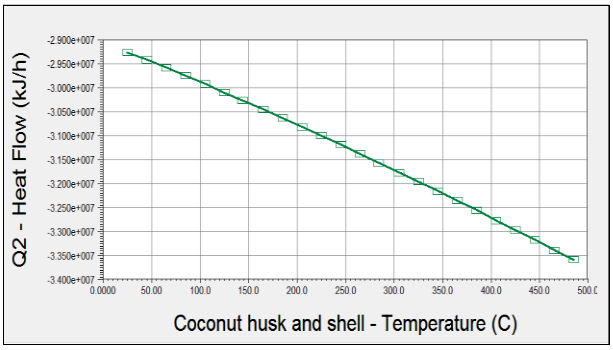


Fig.6: Effect of coconut shell and husk temperature on combustor heat flow (Q2)

(e) Effect of cooled alkane temperature on heat flow in distillation column: Figure 7 represented that less heat would be liberated and Fig. 8 represented that more heat would be required if the alkanes were cooled to a higher extent before fed to the distillation column. But at the same time Fig. 3 impliedthat a higher temperature yielded a higher flow of the lower carbon low cost petroleum.

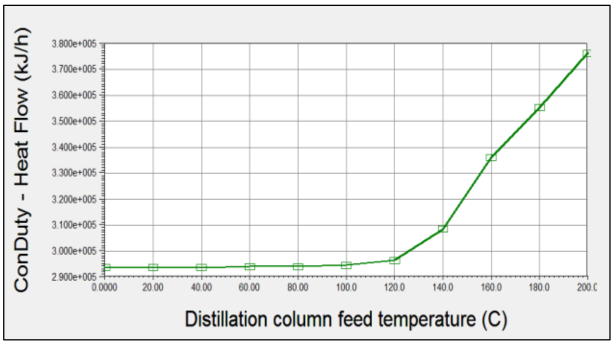


Fig.7: Effect of cooled alkane temperature on heat flow in in total condenser

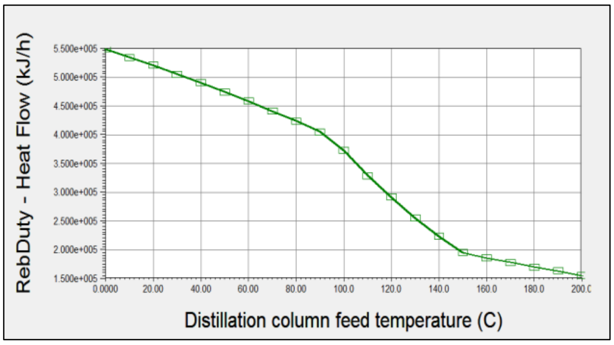


Fig.8: Effect of cooled alkane temperature on heat flow in partial reboiler

5.3 Results from optimization

Initially profit was calculated to be \$ 6987 per hour and \$ 6.12×10^{7} per year at the given process condition. Profit maximization for this simulation was performed considering temperature of the heated air, molar flow rate of mixed air, feed temperature of the distillation column and purity of propane and n-Hexane as the primary variables. After optimization, molar flow rate of propane was decreased and n-Hexane wasincreased. The maximum profit of \$ 7370 per hour and \$ 6.456×10^{7} per year were obtained as shown in Table 2.Theproducts propane and n-hexane thus obtained were 99% pure at the optimized condition.

Table 2: Annual profit calculation after optimization

Product	Production rate (m^3/h)	Unit Cost (\$/m^3)	Price(\$)
Propane	0.9548	845.34	807
n-hexane	0.9950	8794.42	8750
Total selling price			***9557***
Energy stream	Duty (kWh)	Unit Cost (\$/kWh)	Price(\$)
Q1	566.90	0.12	68.03
Q2	370.40		44.44
Q3	1429.00		171.48
Q4	1.83×10^{-3}		2.19×10^{-4}
Q5	1035.00		124.2
Q6	44.07		5.288
Q7	2327.00		279.2
Q8	2509.00		301.1
Q9	2859.00		343.1
Q10	246.20		29.55
Q11	99.56		11.95
Con Duty	88.11		10.57
Reb Duty	45.00		5.40
Raw Material	Amount (kg/h)	Unit Cost (\$/kg)	Price(\$)
Coconut husk and shell	4803	0.165	792.6
Total Cost			***(2187)***
Profit			**7370**
Annual Profit			***6.456×10^{7}***

6. CONCLUSION

The paper studied the feasibility of the Fischer- Tropsch process and it was seen that the plant is market-sustainable and profitable. The annual profit and the product purity of the presented study suggested the process to be a promising alternative to the use of non-renewable energy resources, producing clean fuel to meet the increasing global energy demand. The results represented the optimum process conditions and the appropriate pathway for the production of petroleum products from coconut husks and shells. These and the graphical relations of the process variables could serve as efficient tools in designing a FT synthesis plant for the specified raw material.

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8. NOMENCLATURE

Symbol	Meaning	Unit
P	Profit	dollar($)
V_P	Volumetric flow of propane	(m^3/h)
V_H	Volumetric flow of n-Hexane	(m^3/h)
M_f	Mass flow coconut husk and shell	(kg/h)
Q_i	Heat flow	(kW)