

## Turning Waste into Wealth: A Conceptual Design of Limonene Production Plant from Waste Rubber Tyre

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### ABSTRACT

*Limonene production represents a compelling opportunity in the global market, given its competitive landscape dominated by a few key players who control nearly half of the industrial-grade limonene market. Due to the high polyisoprene content in vehicle tyres, along with the rising number of waste rubber tyres, the production of limonene by pyrolysis of tyres may represent a future trend to turn waste into wealth. Hence, a conceptual plant design was carried out to determine the feasibility of limonene production from waste rubber tyres in Malaysia. This feasibility study involved Aspen Plus simulation and illustrated the main processes using Process Flow Diagram (PFD), Piping and Instrumentation Diagram (P&ID), and comprehensive stream table integrating material and energy balances. The desired product, which is limonene, was produced by the gas-solid pyrolysis within a conical spouted bed reactor (CSBR) in an inert atmosphere of non-oxidizing, achieving limonene of 98% purity. Besides, process optimization via pinch analysis has been performed to recover 223.84 kWh of energy using heat integration, resulting in 62.06% of energy saving. From the economic analysis conducted, the total capital investment is RM12.9 million and the annual revenue is RM124.7 million with an annual limonene production of 543.1 tons. The financial analysis demonstrated a robust return on investment (ROI) of 303%, a simple payback period of 0.33 years and a Net Present Value (NPV) of RM 432.2 million.*

*Keywords: Waste rubber tyre; Limonene; Conceptual plant design; Process optimization; Economic analysis*

### INTRODUCTION

Generally, limonene is available in two grades: food grade and industrial grade. According to the US Food and Drug Administration (FDA), food-grade limonene is considered safe for used in food as it falls under the “Generally Recognized as Safe (GRAS)” list. It finds extensive application in the food and beverage industry as a food additive, serving as a flavouring and sweeteners. Food-grade limonene can be added into pastries, ice cream, puddings, candy, gelatin, chewing gum, and drinks to impart a lemony flavour. Furthermore, it can be employed as a fragrance in perfumes and soaps (Bacanli 2020). Due to its anti-inflammatory and antioxidant properties, food-

grade limonene can also be used in the formulation of various drugs.

On the other hand, industrial-grade limonene finds application in several industries including household cleaning, paint and coating, and the automotive sector. In the household cleaning industry, limonene can be added to products such as carpet cleaners, countertop cleaners, floor cleaners, laundry detergents, and paintbrush cleaners. Similarly, in the automotive industry, limonene is incorporated into products such as brake cleaners, car wash concentrate, engine degreasers, wheel cleaners, and upholstery cleaners (Florida Chemical Company 2021).

Limonene is typically derived from citrus fruits, making citrus-derived limonene the primary source for meeting global demand (Danon et al. 2015). However, the

supply of citrus fruits is highly susceptible to agricultural vulnerabilities and seasonal fluctuations. Consequently, the supply of citrus-derived limonene is unstable and is expected to decrease drastically after the citrus season. In response, the waste-to-wealth concept is proposed. The modern world generates a vast array of waste, including agricultural waste (Kamarudin et al. 2018) and palm oil mill effluent (POME), which can be transformed into valuable product like biogas (Chung et al. 2020). To address the production of value-added chemicals like limonene, waste rubber tyres, which are abundant in Malaysia, would be a great feedstock. Light vehicle tyres (LVT) and heavy vehicle tyres (HVT) are particularly desirable for their higher limonene yield due to their high natural rubber content. About 17 million tonnes of used tyres are generated annually. Tyres consist primarily of 60 to 65 wt% of rubber and 25 to 30 wt% of carbon black. It is essential to select an appropriate disposal method for managing non-biodegradable waste tyre to mitigate environmental concerns (Arabiourrutia et al. 2020).

The current methods for managing waste rubber tyres include direct disposal (landfilling), material recovery (crumbling or retreading) and energy recovery (direct incineration). Generally, these methods fall short in addressing the issue for several reasons. Firstly, the typical design of rubber tyres causes them to be bulky, taking up a significant amount of space while their inside remains hollow. Water tends to accumulate in the hollow side of the waste tyres, creating ideal habitats for parasites and insects that can spread disease. Therefore, if used tyres are left abandoned for an extended period in landfills, they can eventually pose environmental and health risks. Additionally, it is known that used tyres have high combustibility but low flammability. They are typically hard to ignite but burn rapidly, emitting a huge amount of heat and toxic gases once ignited. If tyres in landfills are exposed to an ignition source, the heat and toxic gases emitted during combustion can significantly pollute the environment (Islam et al. 2011). As for the material and energy recovery pathways, the use of waste tyres also comes with significant drawbacks. While the crumbling of waste rubber tyres does not directly harm the environment, the recycling process is highly energy-intensive, leading to high operation costs. Despite having a lower selling price compared to new rubber products, the quality of retreaded tyres or products made from recycled tyres is often inferior to new product. As a result, the low quality-to-price ratio limits market demand (Mulaudzi 2017). Meanwhile, direct incineration of waste tyres is typically carried out due to their high calorific value, but the combustion process invariably produces harmful emissions that pose threats to the environment and human health.

Producing limonene from waste rubber tyres offers a potential solution to address both the problems of excessive waste rubber tyres and seasonal limonene shortage simultaneously. The feasibility of this opportunity will be investigated in this study. The raw material used is waste rubber tyre crumbs and the desired product is limonene. The plant's target production output is 532,227 kg of limonene per year, with a purity of 98%.

## METHODOLOGY

### PROCESS ROUTE SELECTION

A thorough comparison has been conducted among three different process routes: atmospheric gas-solid pyrolysis using a conical spouted bed reactor (CSBR), vacuum pyrolysis using a moving stirred bed reactor, and fast pyrolysis using continuous rotary kiln reactor. Out of these three options, gas-solid pyrolysis in an inert, non-oxidising environment using CSBR, as illustrated in Figure 1, has been selected. This selection is based on considerations of sustainability, energy efficiency, and environmental impact. Today, the pyrolysis of used rubber tyres presents a practical solution to the widespread issue of tyre waste disposal at undesignated sites. This high-value-added technology generates useful outputs such as gas, fuel oil, carbon black, and scrap steel, making pyrolysis an energy self-sufficient process as the products produced fulfill the plant's energy need. Nitrogen gas acts as the fluidising agent, preventing the burning of pyrolyser and enhancing heat transfer. Besides, the use of CSBR facilitates the handling of sticky and irregular materials, such as used rubber tyres. Additionally, CSBR allows for vigorous gas-solid contact, improving mass and heat transfer between phases. The higher solid heating rate contributes to the creation of an isothermal bed, preventing bed fluidization due to particle agglomeration. Cyclic particle movement in the spouted bed prevents bed defluidisation caused by particle agglomeration and localized overheating. Moreover, continuous gas-solid pyrolysis results in a higher yield of light aromatics. Additionally, this continuous operation mode offers benefits such as reduced material handling, higher productivity, cost-effectiveness and better quality control. Furthermore, the process operates at ambient pressure, reducing equipment cost and operating costs.

The yield of limonene (20.4 wt%) surpasses that of other process routes. Furthermore, gas-solid pyrolysis at lower temperatures (425 °C) using CSBR increases the yield of desired products. Lower temperature contributes to a reduction in thermal energy demand, ultimately

reducing operational cost. Importantly, the pyrolysis plant does not emit toxic or greenhouse gases, thanks to the absence of oxygen and the low operating temperatures, which prevent the production of pollutants such as dioxins and furans. This can prevent the spread of respiratory illnesses and combat climate change in the region (Oliveira Neto et al. 2019). This technology promotes the circular economy by enabling the complete recycling of all used

tyres, leaving no residual waste. Moreover, the maintenance costs for gas-solid pyrolysis are affordable compared to other process routes. Ultimately, gas-solid pyrolysis emerges as a practical, sustainable, and environmentally friendly option for waste tyre disposal. It offers significant benefits in terms of energy savings, material recovery, and the production of high-value commodities.

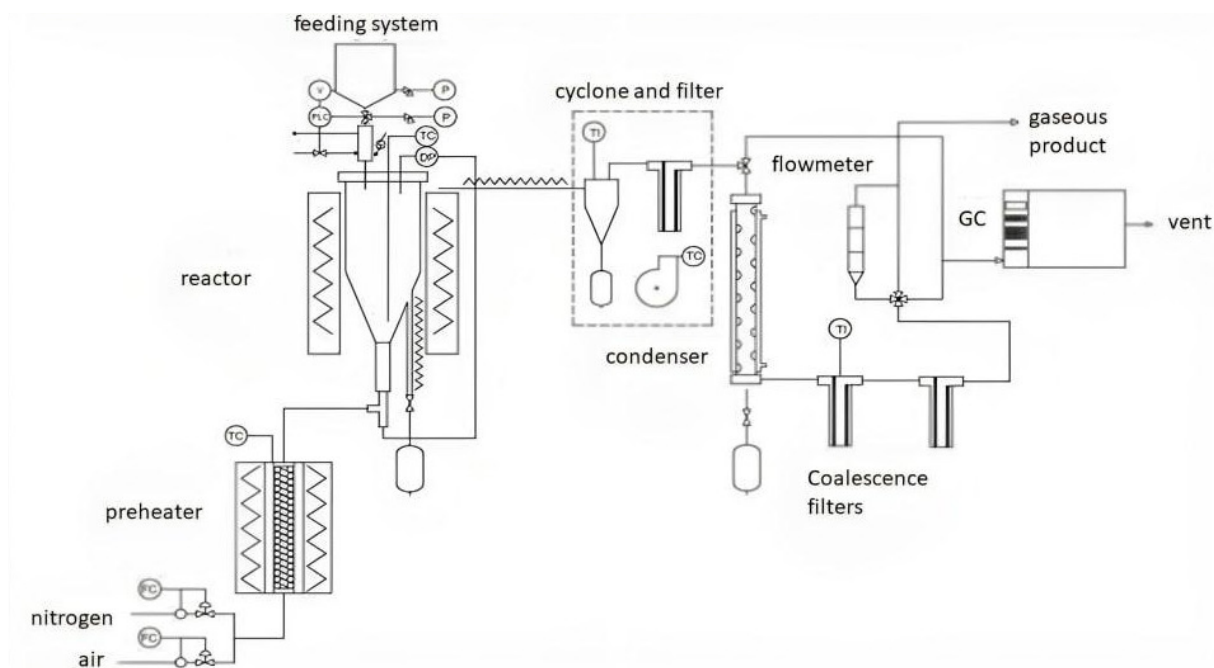


FIGURE 1. Scheme of pilot plant continuous gas-solid pyrolysis with CSBR  
Source: Arabiourrutia et al. (2020)

## PROCESS DESIGN AND SYNTHESIS

### LEVEL 1: PROCESS OPERATING MODE

The Onion Model process design hierarchy has been used in the conceptual design of the limonene production pyrolysis process from waste rubber tyres. At the first level of this hierarchical approach, the selection of the process operating mode is made. The process operating mode encompasses various aspects of a plant's lifecycle, including start-up, normal operation, shutdown, equipment cleaning and decontamination, and maintenance phases. In this case, atmospheric gas-solid pyrolysis of waste tyres through continuous feeding into a CSBR has been selected. When designing the chemical process, continuous operating mode was preferred over batch operating mode. This is due to the several advantages offered by the

continuous operation mode such as time-saving, reduced material handling, higher productivity, lower production costs, and improved quality control.

### LEVEL 2: INPUT-OUTPUT STRUCTURE OF THE PROCESS

The input-output structure of the waste rubber tyre pyrolysis process is shown in Figure 2, while Table 1 summarizes the pyrolysis reactions that occur during the process. In the production of limonene, shredded waste rubber tyres are used as the raw materials while nitrogen serves as the inert fluidising gas. Limonene, which has a boiling point of 177.25°C, is the main product of the chemical process. At the same time, by-products such as tyre pyrolysis oil (TPO) and char are also generated. Non-condensable gases, containing nitrogen gas and hydrocarbons, will undergo treatment before discharge.

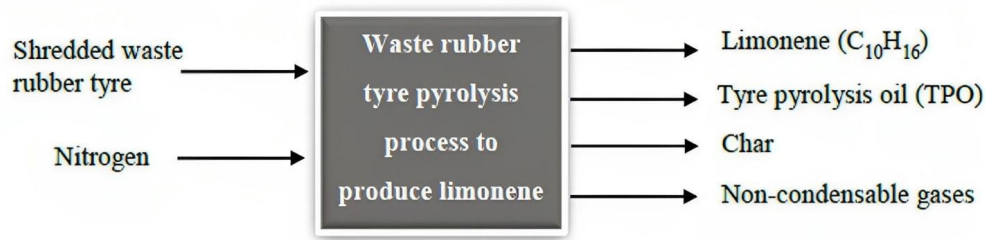


FIGURE 2. Input-output structure for the production of limonene from waste rubber tyres

TABLE 1. Pyrolysis reactions and the yield of each component (Ismail et al., 2017)

Products	Reactions	Yield (wt%)
Methane (CH <sub>4</sub> )	$C + 2 H_2 \rightarrow CH_4$	0.06
Ethane (C <sub>2</sub> H <sub>6</sub> )	$2 C + 3 H_2 \rightarrow C_2H_6$	0.08
Ethylene (C <sub>2</sub> H <sub>4</sub> )	$2 C + 2 H_2 \rightarrow C_2H_4$	0.1
Propane (C <sub>3</sub> H <sub>8</sub> )	$3 C + 4 H_2 \rightarrow C_3H_8$	0.20
Propylene (C <sub>3</sub> H <sub>6</sub> )	$3 C + 3 H_2 \rightarrow C_3H_6$	0.09
Isobutylene (C <sub>4</sub> H <sub>8</sub> )	$4 C + 4 H_2 \rightarrow C_4H_8$	1.28
2-methyl-1,3-butadiene (C <sub>5</sub> H <sub>8</sub> )	$5 C + 4 H_2 \rightarrow C_5H_8$	6.67
Benzene (C <sub>6</sub> H <sub>6</sub> )	$6 C + 3 H_2 \rightarrow C_6H_6$	1.16
Toluene (C <sub>7</sub> H <sub>8</sub> )	$7 C + 4 H_2 \rightarrow C_7H_8$	1.86
Styrene (C <sub>8</sub> H <sub>8</sub> )	$8 C + 4 H_2 \rightarrow C_8H_8$	10.01
1-methyl-2-ethylbenzene (C <sub>9</sub> H <sub>12</sub> )	$9 C + 6 H_2 \rightarrow C_9H_{12}$	4.7
d-limonene (C <sub>10</sub> H <sub>16</sub> )	$10 C + 8 H_2 \rightarrow C_{10}H_{16}$	30.56
Benzothiazole (C <sub>7</sub> H <sub>5</sub> NS)	$7 C + 2.5 H_2 + 0.5 N_2 + S \rightarrow C_7H_5NS$	5.55
n-hexadecane (C <sub>16</sub> H <sub>34</sub> )	$16 C + 17 H_2 \rightarrow C_{16}H_{34}$	2.01
n-nonadecane (C <sub>19</sub> H <sub>40</sub> )	$19 C + 20 H_2 \rightarrow C_{19}H_{40}$	1.77
Char	-	33.9

### LEVEL 3: REACTOR DESIGN AND REACTOR NETWORK SYNTHESIS

Reactor design and reactor network synthesis represent the third levels of the hierarchical process design. In the pyrolysis process, waste rubber tyres are thermally decomposed into limonene. CSBR is chosen for this process because it can handle the sticky and irregular shape of waste rubber tyres better. Besides, CSBR facilitates vigorous gas-solid contact, preventing particle agglomeration and, consequently, bed defluidisation (López et al. 2010). The reactor will operate at 425 °C and 1 atm without the need for a catalyst. Throughout the pyrolysis processes, nitrogen gas will serve as the purge gas to maintain an inert atmosphere within the reactor. Due to the process complexity, this study focuses on components with significant composition only. In particular, six components in gaseous products (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>), six components in oil products (C<sub>5</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>7</sub>H<sub>8</sub>, C<sub>8</sub>H<sub>8</sub>, C<sub>9</sub>H<sub>12</sub>, C<sub>10</sub>H<sub>16</sub>), three components in tar products (C<sub>7</sub>H<sub>5</sub>NS, C<sub>16</sub>H<sub>34</sub>, C<sub>19</sub>H<sub>40</sub>), and char are

selected for consideration (López et al. 2010). Table 1 displays the yield of various gaseous products, liquid products, and chars while Figure 3 illustrates the geometry of CSBR and Table 2 lists its properties.

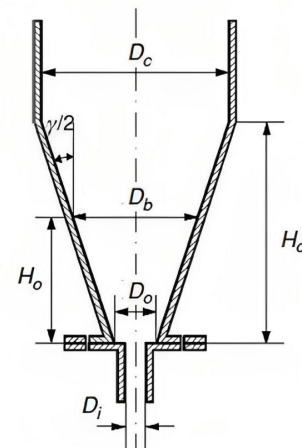
FIGURE 3. Geometry of conical spouted bed reactor  
Source: Arabiourrutia et al. (2020)

TABLE 2. The properties of conical spouted bed reactor

Dimensions	Notation	Value	Unit
Inlet diameter	$D_i$	0.2076	m
Cone bottom diameter	$D_o$	0.2966	m
Static bed upper diameter	$D_b$	0.7042	m
Cylindrical column diameter	$D_c$	2.5102	m
Solid outlet diameter	$D_s$	0.2191	m
Static bed height	$H_o$	0.5599	m
Solid outlet height from gas inlet	$H_s$	1.9	m
Conical height	$H_c$	2.8589	m
Cylindrical height	$H_{cyl}$	2.3359	m
Total height	$H_T$	5.1948	m
Cone angle		40	°

## LEVEL 4: SEPARATION SYSTEM SYNTHESIS

The desired product, limonene, must be separated from the TPO produced in the pyrolysis process. The primary constituents of the light and medium components of TPO are alkylated naphthalenes, alkylated benzenes, alkanes and alkenes (Danon et al. 2015). According to TPO distillation curves, 50 wt% of the oil is distilled below 200 °C (light naphtha fraction). Limonene typically exists in TPO at a concentration of 10 wt% with a normal boiling point ranging from 60 °C to 200 °C (Danon et al. 2015). To achieve high limonene purity of 98%, the separation system proposed in this design comprises a cyclone, a flash drum, three distillation columns and accessory units, including pumps and heat exchangers. After pyrolysis, volatile pyrolysis products are separated from the solid char in the CSBR. The volatile products are then directed to a cyclone (C-601) for further separation of fine char particles. The solid char particles from both units are being collected. Subsequently, the volatile products are cooled from 425 °C to 25 °C using a series of heat exchangers in the heat integration system (H-601, H-602, H-603, H-604, H-605, L-601). Following the cooling process, the stream is directed to a knockout drum (K-601) operating at 100 kPa to separate most of the limonene from the other products. From the knock-out drum, the stream with a significant amount of limonene is sent into a pump (P-601), while the remaining stream is directed for waste treatment. In this study, high purity limonene is desired as it can be utilised in various application such as household, institutional, and industrial product formulations (Florida

Chemical Company 2006). Hence, three distillation columns are used to purify the limonene obtained from the knock-out drum. Before the stream enters the first distillation column (D-601), a pump (P-601) is used to pressurise it to approximately 200 kPa. This facilitates the easier flashing of lighter components when the stream enters a low-pressure zone. The pressurised stream is then heated to 111 °C using two heat exchangers (H-606 & H-608) to ease the fractionation of a limonene-rich fraction. In the first distillation column, the *i*-pentene-enriched naphtha fraction (bottom product) is separated from other lighter components and non-condensable gases, allowing for the avoidance of refrigerants and high-pressure operation in this configuration (Mulaudzi 2017). Subsequently, the limonene-rich fraction is pumped into the second and third distillation columns (D-602 and D-603) to achieve a final limonene purity of 98%.

## LEVEL 5: HEAT INTEGRATION

In 1981, Kinhoff and Turner presented the Pinch analysis or Pinch Design Method (PDM). Based on a predetermined set of principles, it serves as a methodical way to build a heat exchanger network. Utility exchangers, such as heaters and coolers, are only added when the integration of heat exchangers is insufficient to provide the appropriate temperature. Data such as supply temperature ( $T_s$ ), target temperature ( $T_t$ ), and heat duty of the streams are needed for the pinch analysis, and the information is given in Table 3.



TABLE 3. Stream information

Stream	Supply Temperature, $T_s$ (K)	Target Temperature, $T_t$ (K)	Heat Duty (kW)
Cold 1 (S2 – S3)	293.15	698.15	108.499
Cold 2 (S14 – S15)	298.15	384.15	6.0969
Hot 1 (S9 – S11)	698.15	298.15	-158.047
Hot 2 (S21 – S24)	450.01	308.15	-6.0176
Hot 3 (S23 – S25)	507.25	333.15	-2.5605
Reb 1	458.20	458.20	28.8919
Reb 2	510.79	510.79	8.2436
Reb 3	468.81	468.81	7.0172

As shown in Table 3, the network will only contain the distillation columns reboilers. The Correct Integration approach is used to determine whether the distillation columns should be fully or partially integrated into the background process by weighing the possible energy savings (Gundersen, 2017). The three primary causes of Correct Integration are listed below:

Case 1:  $T_{reb} > T_{cond} > T_{pinch}$

The condenser of the distillation column needs to be integrated into the background process above Pinch.

Case 2:  $T_{reb} > T_{pinch} > T_{cond}$

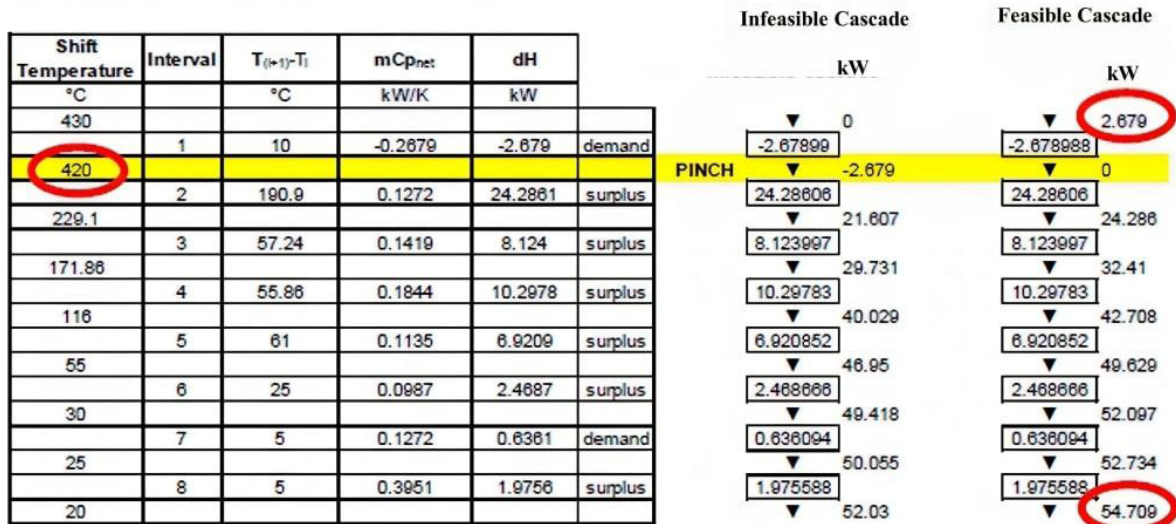
As there will be no energy savings, the distillation column should not be incorporated into the background process.

Case 3:  $T_{pinch} > T_{reb} > T_{cond}$

The reboiler of the distillation column needs to be integrated into the background process below Pinch.

The pinch temperature, which was calculated by taking into account a background process with two cold streams

TABLE 4. Cascaded problem table involving default background process only



and three hot streams, was determined to be 420 °C (693.15 K). After comparing the temperature of all the reboilers and condensers, the pinch temperature was discovered to fall under Case 3. Hence, the heat exchanger network solely contains reboilers and does not include condensers. The cascaded problem tables of pinch analysis for the background process alone and the background process and reboiler are shown in Tables 4 and 5, respectively.

According to Table 4, the default background process's minimum hot and cold utilities are 2.68 kW and 54.71 kW, respectively, adding up to 57.39 kW. The total utility will be 136.84 kW when the utilities needed for the reboilers (44.15 kW) and condensers (35.30 kW) that were not included in the analysis are added. The minimum hot and cold utilities are 16.86 kW and 24.74 kW, respectively, adding up to 41.60 kW after incorporating all the reboiler.

This indicates that reboilers will increase the amount of energy saved by a heat exchanger network. After accounting for the utility of the condensers that were eliminated, the total amount of energy needed was 76.90 kW. Table 6 provides a summary of the utilities in various configurations. Without heat integration, the original system required 158.75 kW of hot energy and 201.93 kW of cold energy, for a total of 360.68 kW of energy. However, 78.68% of the energy is saved following the heat integration. Figures 4 and 5 display the composite and grand composite curves from the Pinch analysis. Without heat integration, the original system required 158.75 kW of hot energy and 201.93 kW of cold energy, for a total of 360.68 kW of energy. However, 78.68% of the energy is saved following the heat integration. Figures 4 and 5 display the composite and grand composite curves from the Pinch analysis.

TABLE 5. Cascaded problem table involving background process integrated with reboilers

Shift Temperature °C	Interval	$T_{(i+1)}-T_i$ °C	$mCp_{net}$ kW/K	dH kW	
430					
	1	10	-0.2679	-2.679	demand
420					
	2	177.36	0.1272	22.5635	surplus
242.64					
	3	1	-8.1168	-8.1168	demand
241.64					
	4	12.54	0.1272	1.5953	surplus
229.1					
	5	28.44	0.1419	4.0365	surplus
200.66					
	6	1	-8.8751	-8.8751	demand
199.66					
	7	9.61	0.1419	1.3639	surplus
190.05					
	8	1	-28.7501	-28.7501	demand
189.05					
	9	17.19	0.1419	2.4398	surplus
171.86					
	10	55.86	0.1844	10.2978	surplus
116					
	11	61	0.1135	6.9209	surplus
55					
	12	25	0.0987	2.4687	surplus
30					
	13	5	0.1272	0.6361	demand
25					
	14	5	0.3951	1.9756	surplus
20					

	Infesible Cascade	Feasible Cascade
	kW	kW
	0	16.862
	▼ -2.67899	▼ -2.678988
	-2.679	14.183
	▼ 22.56351	▼ 22.56351
	19.885	36.746
	▼ -8.11678	▼ -8.116781
	11.768	28.629
	▼ 1.595323	▼ 1.595323
	13.363	30.225
	▼ 4.036451	▼ 4.036451
	17.4	34.261
	▼ -8.87507	▼ -8.875071
	10.524	27.386
	▼ 1.363935	▼ 1.363935
	11.888	28.75
	▼ -28.7501	▼ -28.75007
	PINCH -16.862	0
	▼ 2.439754	▼ 2.439754
	-14.422	2.4398
	▼ 10.29783	▼ 10.29783
	-4.1241	12.738
	▼ 6.920852	▼ 6.920852
	2.7968	19.658
	▼ 2.468666	▼ 2.468666
	5.2654	22.127
	▼ 0.636094	▼ 0.636094
	5.9015	22.763
	▼ 1.975588	▼ 1.975588
	7.8771	24.739

TABLE 6. Energy saving after integration of heat exchanger network

Design	Hot Utility (kW)	Cold Utility (kW)	Total Utility (kW)	Energy Saving (kW)	Percentage of Saving (%)
Background process	46.83	90.01	136.84	223.84	63.06
Background process + reboiler	16.86	60.04	76.90	283.78	78.68

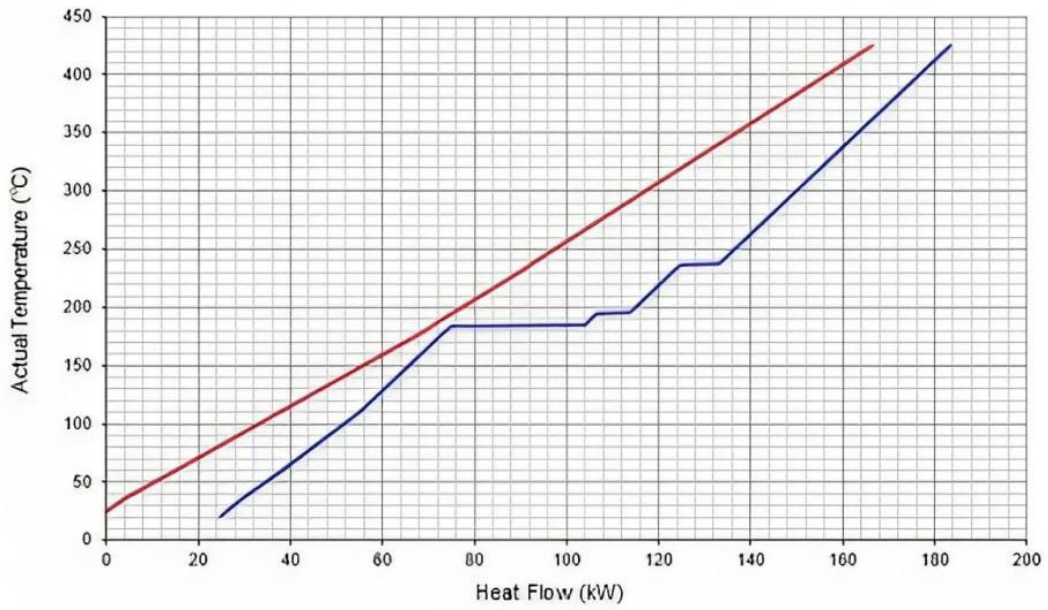


FIGURE 4. Composite curve of pinch analysis including reboilers

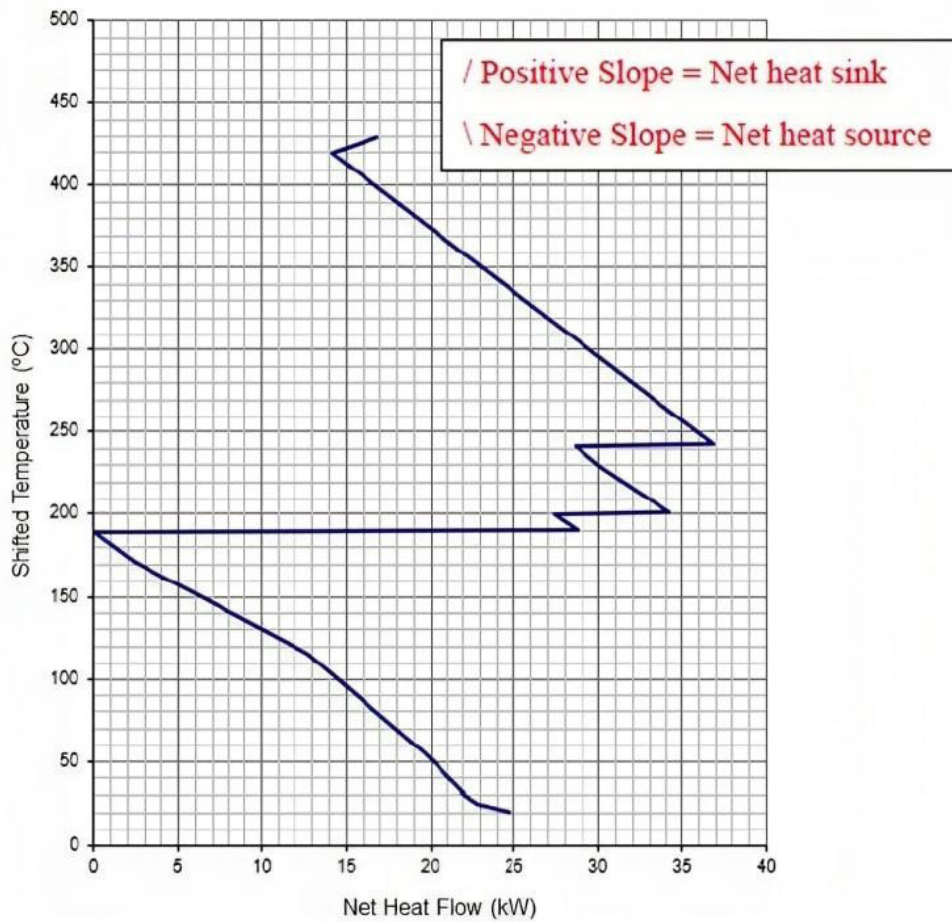


FIGURE 5. Grand composite curve of pinch analysis including reboilers



## PROCESS MECHANISM

According to Singh et al. (2018), light vehicle tyres (LVT) and heavy vehicle tyres (HVT) have a significantly higher content of natural rubber as compared to medium vehicle tyres (MVT). Since the main source of limonene from the waste tyre is the content of natural rubber, also known as polyisoprene, LVT and HVT is expected to have a higher limonene yield. Gowda (2018) proved that LVT and HVT have higher limonene yield through a gas chromatography-mass (GC-MS) analysis of the TPO obtained from waste tyres of motorcycles (LVT), cars (MVT), and trucks (HVT). The estimated limonene yields were 29.54%, 13.79%, and 28.78% respectively. The poor limonene yield of MVT is due to its composition, which encourages the conversion of limonene and other heavy hydrocarbons to lighter

hydrocarbons. As a result, LVT and HVT are preferred for our application.

Pyrolysis of waste rubber produces a variety of thermal decomposition byproducts. Because polymer radicals often combine to form hexahydric ring compounds, limonene is one of the products of the scission of polymer chains (Zhang et al. 2008). Monomer isopentane is another primary byproduct of pyrolysis in addition to dimer limonene. Then, limonene can be produced from isoprene monomers through a secondary pathway, the Diels-Alder cyclisation reaction (Zhang et al. 2008). Figure 6 shows the two pyrolysis methods that turn natural rubber into limonene. In addition, Figure 7 illustrates a different, related method that produces limonene. This mechanism begins with the polymerization of isoprene to form dimeric species, followed by the cyclization of the resultant diradical species, and then a two-step pyrolysis isomerization (Rofiqul et al. 2007).

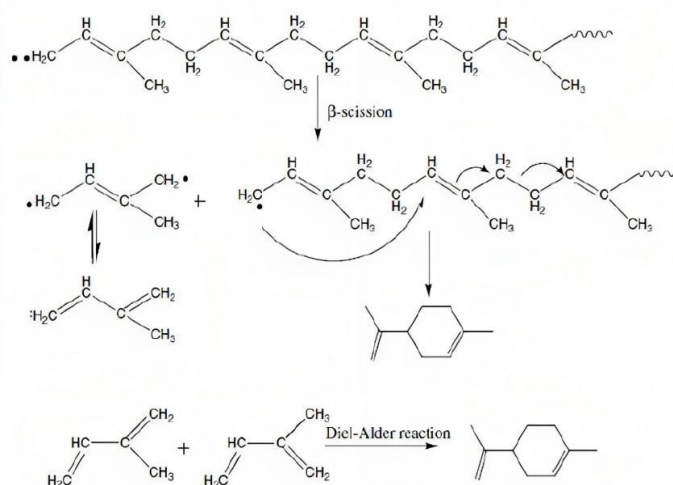


FIGURE 6. Two mechanisms of pyrolytic decomposition of natural rubber to limonene  
 Source: Zhang et al. (2008)

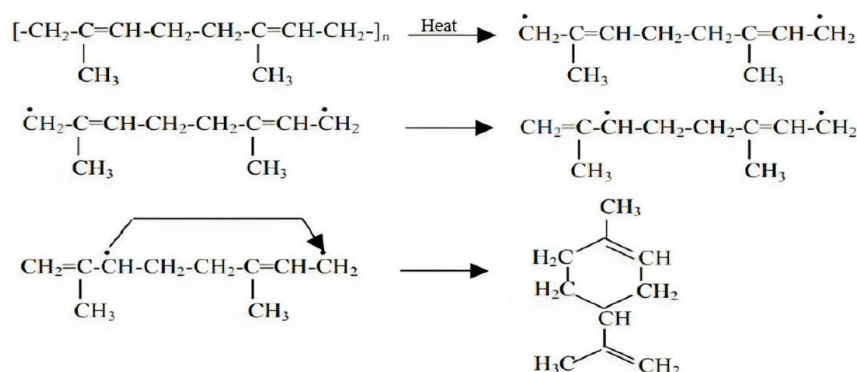


FIGURE 7. Mechanism of the pyrolytic decomposition of natural rubber to propylene and its isomerisation into limonene  
 Source: Rofiqul et al. (2007)

RESULTS AND DISCUSSION

ASPEN PLUS FLOWSHEET SIMULATION

The processing units and operating conditions in the whole process are initially referring to the Aspen modelling done by Mulaudzi (2017), and will subsequently be optimized to obtain the maximum limonene production. The process flowsheet simulation of the limonene production plant is shown in Figure 8. According to Table 7, the models involved in a simulation of the 15 operational units are RYield, RadFrac, Cyclone, Flash2, Mixer, Sep, Heater, and Pump. The labels of the equipment shown in Table 7 will be used in the following description.

Table 8 displays the outcome of the manually executed mass balance analysis as well as the Aspen simulation for the pyrolyser. The amount of variance between the element’s mass flows calculated using a manual method and Aspen Plus fluctuates between 0% to 3.33 %. The

acceptable amount is typically from the 5% threshold. The two Aspen Plus simulations and calculation by hand effectively generated 68.57 kg/h of limonene with a 98 wt% purity, meeting the required quantity and quality.

The DECOMP, PYROLYSE, and SEP1 instruments are used to separately model the reactor through Aspen Plus. Upon completing an Excel energy balance calculation, the process’s enthalpy is calculated as one (1) because they are a single unit, and it is represented by the symbol REACTOR. The determined enthalpy is compared to the combined thermal duty of DECOMP, PYROLYSE, and SEP1 by Aspen Plus. Pumps need an electrical source because their positive function indicates that they acquire energy in order to function. Comparing the total heat duty of the three distillation columns (D1, D2, and D3), it can be seen that D1 consumes the most energy when compared to the other columns. Every piece of equipment has energy balances that are manually performed and Aspen energy balances that differ by less than 20%, which is within the acceptable range.

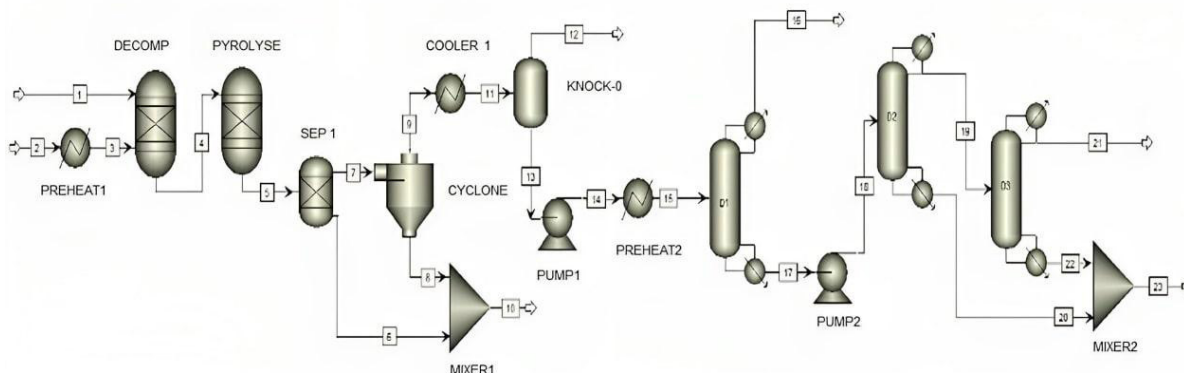


FIGURE 8. Aspen Plus flowsheet simulation

TABLE 7. Summary of the models used in simulating operation units

Model	Equipment
Heater	PREHEAT1, COOLER1, PREHEAT2
Reactor	DECOMP, PYROLYSE
Separator	SEP1
Cyclone	CYCLONE
Distillation tank	D1, D2, D3
Flash tank	KNOCK-D
Mixer	MIXER1, MIXER2
Pump	PUMP1, PUMP2

TABLE 8. Mass balance results at the Pyrolyser

Stream	Mass Flow from Manual Calculation (kg/hr)	Mass Flow from Aspen Simulation (kg/hr)	Percentage Difference (%)
Inlet (Stream 4)			
Nitrogen Gas (N <sub>2</sub> )	909.8971	909.8971	0
Carbon (C)	223.50	223.61	0.0483
Hydrogen (H)	18.00	17.87	0.7078
Sulfur (S)	6.75	6.71	0.6561
Nitrogen (N)	1.75	1.81	3.3309
Total Mass Flow (kg/hr)	1159.90	1159.90	0
Outlet (Stream 5)			
Nitrogen Gas (N <sub>2</sub> )	909.8971	909.8971	0
Methane (CH <sub>4</sub> )	0.1500	0.1500	0
Ethane (C <sub>2</sub> H <sub>6</sub> )	0.2000	0.2000	0
Ethylene (C <sub>2</sub> H <sub>4</sub> )	0.2500	0.2500	0
Propane (C <sub>3</sub> H <sub>8</sub> )	0.5000	0.5000	0
Propylene (C <sub>3</sub> H <sub>6</sub> )	0.2250	0.2250	0
Isobutylene (C <sub>4</sub> H <sub>8</sub> )	3.2000	3.2000	0
2-Methyl-1,3-Butadiene (C <sub>5</sub> H <sub>8</sub> )	16.6750	16.6750	0
Benzene (C <sub>6</sub> H <sub>6</sub> )	2.9000	2.9000	0
Toluene (C <sub>7</sub> H <sub>8</sub> )	4.6500	4.6500	0
Styrene (C <sub>8</sub> H <sub>8</sub> )	25.0250	25.0250	0
1-Methyl-2-Ethylbenzene (C <sub>9</sub> H <sub>12</sub> )	11.7500	11.7500	0
d-Limonene (C <sub>10</sub> H <sub>16</sub> )	76.4000	76.4000	0
Benzothiazole (C <sub>7</sub> H <sub>5</sub> NS <sub>2</sub> )	13.8750	13.8750	0
n-Hexadecane (C <sub>16</sub> H <sub>34</sub> )	5.0250	5.0250	0
n-Nonadecane (C <sub>19</sub> H <sub>40</sub> )	4.4250	4.4250	0
Char	84.7500	84.7500	0
Total Mass Flow (kg/hr)	1159.90	1159.90	0
Limonene Purity (wt%)	6.5868	6.5868	0

## ASPEN ENERGY ANALYZER

The programme used to create the heat exchanger system layout is fed with all relevant information, including the three hot flows, two cold flows, the three streams using reboilers, supply and goal temperatures, and heat capacity metrics. Additionally, “Refrigerant 1” and “Very High Temperature” utility flows have been selected to provide exterior refrigeration and heating. Additionally, a 10 K (T<sub>min</sub>) minimum temperature variation is specified. As a consequence, the software generates 10 configurations of heat exchanger networks (HEN). The fifth design is chosen

and used as a guide to create the entire process flow diagram. On the basis of capital expense and HEN complexity, the optimal HEN design is analysed and selected. In this sense, the fifth configuration (Figure 9) featured a less complex HEN than the third configuration (Figure 10), which was more economical yet less expensive. The third structure with the identical quantity of heat exchangers as the fifth structure, had a reduced mean price per heat exchanger. Nonetheless, the HEN of the third design is comparatively more complex, resulting in an intricate flow diagram.

The downstream 17 will have to be cooled from 82.55 °C to 25.00 °C using a single chilling utility heat exchanger.

Typically, the water from the towers of cooling will be utilised as the chilling medium. Nevertheless, the temperature of the chilling water is going to rely heavily on the atmospheric wet-bulb temperature. To obtain a stream with an exit temperature of 25.0 °C, the entry cooling water temperature must be a minimum of 20.0 °C. During the day, the temperature of a wet bulb in Malaysia may decrease to 19.90 °C, but it is typically 25.40 °C. Consequently, conventional towers for cooling are unlikely to be capable to provide chilling waters at 20.00 °C in Malaysia, making this procedure impractical. The solution that is suggested is to use chilled water as opposed to traditional chilling water. The energy cost of refrigerated water is RM0.48/RTh, or RM3.7910-5/kJ, as reported by Bursa Malaysia in 2021. Using the heat duty of 108554.3 kJ/hr, the energy cost of using frigid water as the chilling utility has been projected to be RM98.77 per day or about RM32,595 per year. The temperature of the inlet of chilled water will be 5°C and the discharge temperature will be 20°C, resulting in a required flow rate of 1,729,21 kg/h.

An indirect-fired boiler can be used as the external heating source when the heat produced by the heat exchanger is insufficient to adequately heat the process streams. In this situation, natural gas serves as both a heating source and a fuel for a boiler that heats fuel. The fuel acts as a heat exchanger, transferring the heat generated to the process fluids. The fired heater was chosen because, unlike a steam heating system, which requires a specific level of pressure to operate well, it does not have a pressurised heating system. Therefore, the risk of hazardous accidents in the facility has been eliminated and continuous surveillance and control of system pressure readings are no longer required. To put it another way, the combustion heater can lower maintenance costs and improve workplace safety. Also, heated oil will not cause boiler corrosion. Although water is an inexpensive heating medium, it is susceptible to corrosion; therefore, it requires regular maintenance to remove rust. In addition, since the boiling point of heated oil is higher than that of water, the fired heater may work at greater temperatures while offering efficient heating. In addition, electrical heating is not included because it is appropriate for smaller-batch procedures that utilise non-inflammable substances.

Moreover, because of the thermodynamic inefficiency of power generation, heat from electricity is substantially costlier than heat from fuels. Moreover, electric heating equipment is expensive and requires regular upkeep. Specifically, electric heating is one of the causes of runaway reactions that will result in catastrophic detonation at the plant (Towler & Sinnott 2021).

#### PROCESS FLOW DIAGRAM

Aspen Plus was employed for modelling the pyrolysis process. The plant is comprised of thirty operational components, including heat exchangers, conical spouted bed reactors, cyclones, mixers, knock-out drums, pumps, distillation columns, splitters, coolers, heaters, condensers, and reflux drums. The process flow diagram of the designed pyrolysis system for generating limonene via waste rubber tyres is depicted in Figure 11, in which each stream has its label, temperature, and pressure.

#### PIPING AND INSTRUMENTATION DIAGRAM

In the P&ID, the piping tagged as 0.125"-C<sub>10</sub>H<sub>16</sub>-CS-N, where 0.125" is the nominal size of the pipe or diameter in inches, C<sub>10</sub>H<sub>16</sub> is the elements contained within the pipe, CS refers to carbon steel, indicating the material of construction for the pipe, and N denotes no insulation. The letter "Y" can be used to indicate conduit insulation if it exists. To estimate the conduit size, the formula  $Q = vA$  is used, where Q is the fluid's flow rate in volume (m<sup>3</sup>/s), v is the solid or fluid flow velocity (m/s), and A is the cross-sectional area (m<sup>2</sup>) of the fluid flows. Solid, liquid, and gas streams, respectively, are presumed to have ideal flow velocities of 1 m/s, 1.5 m/s, and 20 m/s. As the pipe's components are non-corrosive, carbon steel was chosen as the construction material for all pipelines. The comprehensive P&ID consists of three distinct sections. Figures 12, 13, and 14 depict Sections 1, 2, and 3.



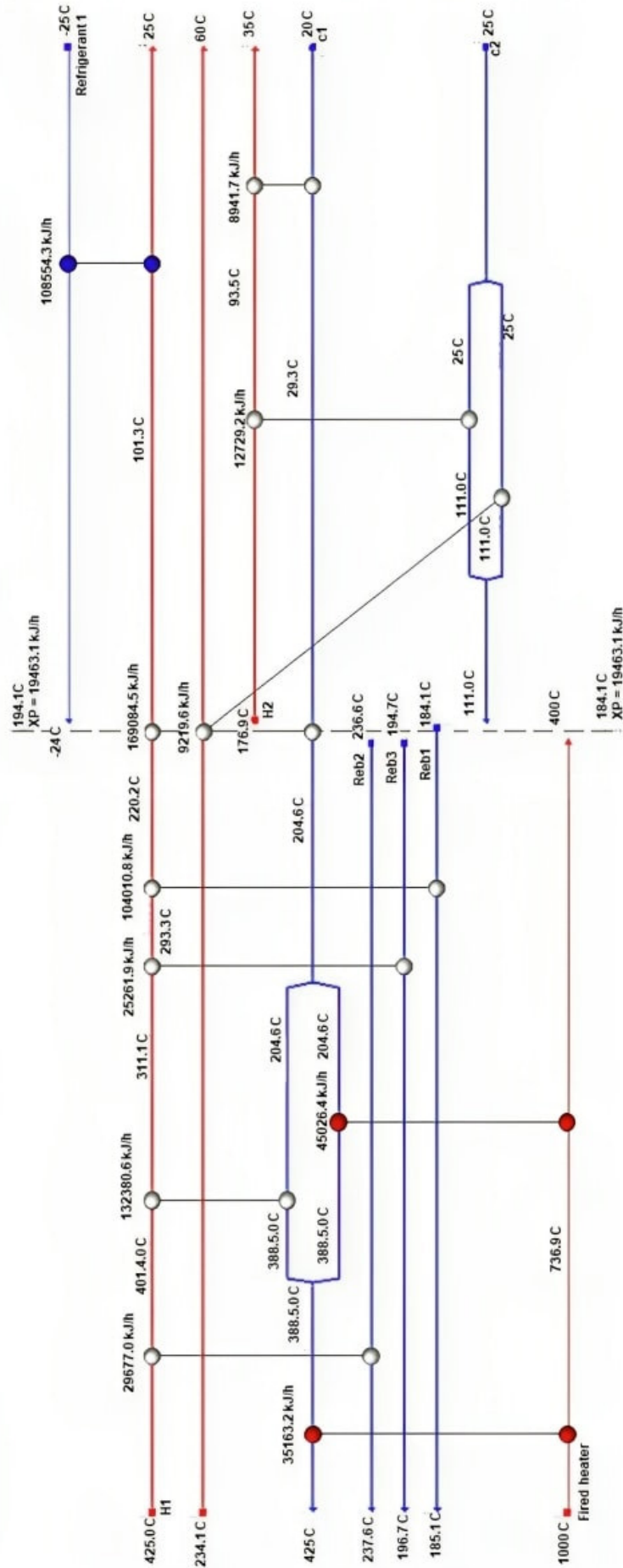


FIGURE 9. Proposed design of heat exchanger network including reboilers (fifth design)

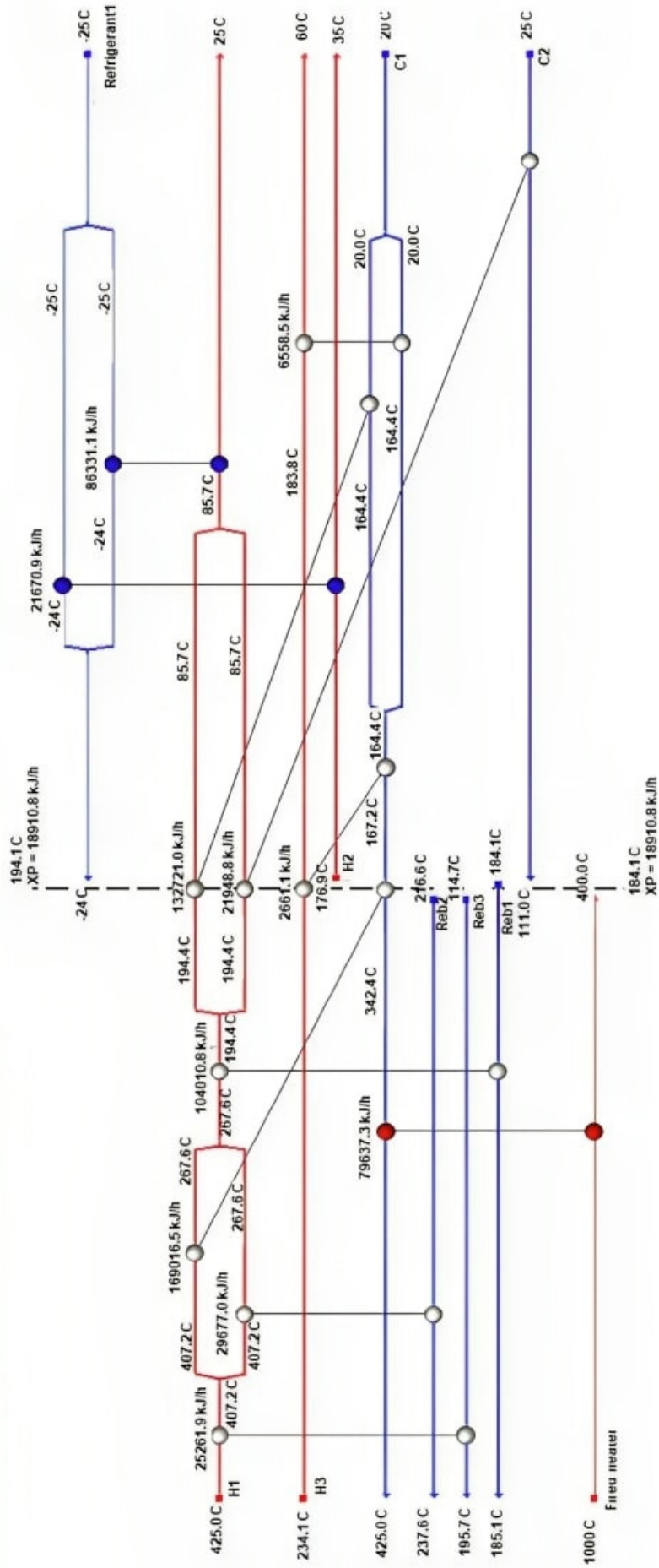


FIGURE 10. Proposed design of heat exchanger network including reboilers (third design)

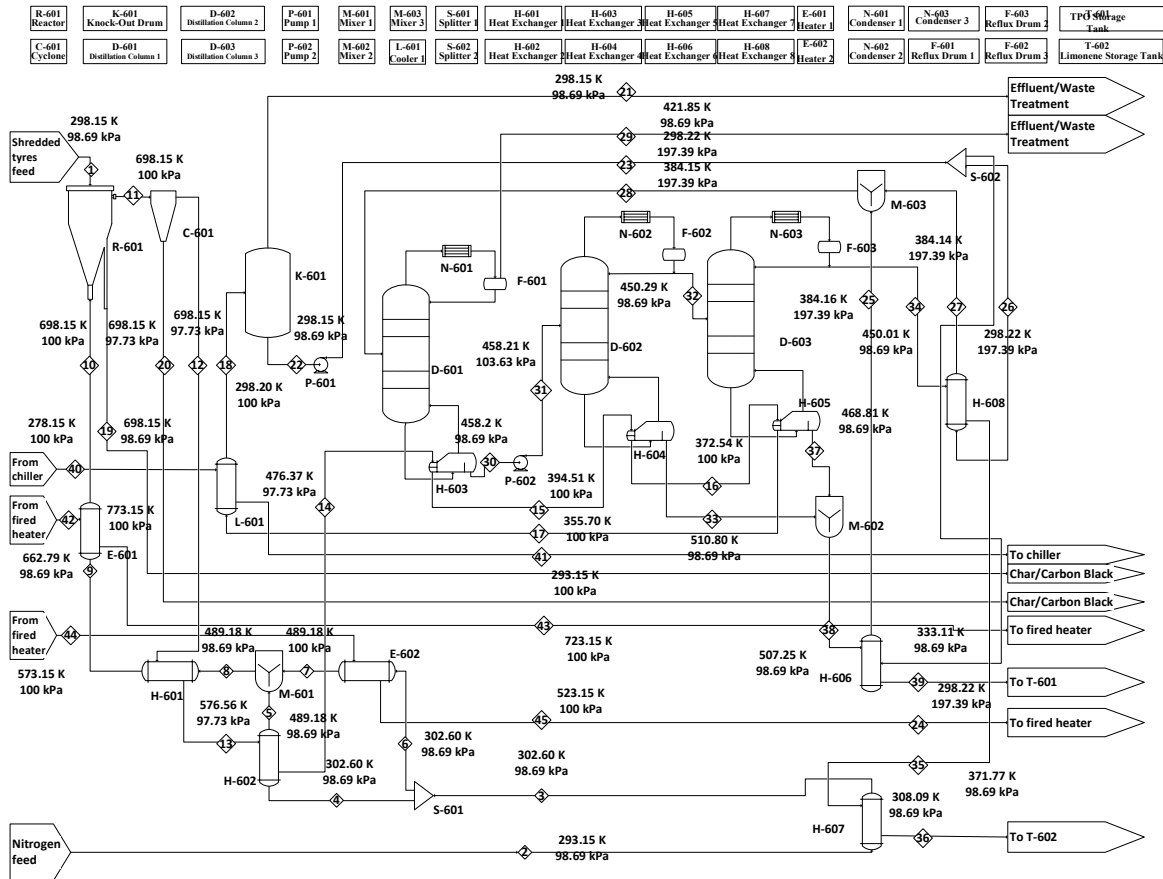


FIGURE 11. Process Flow Diagram (PFD) of the waste rubber tyre pyrolysis plant

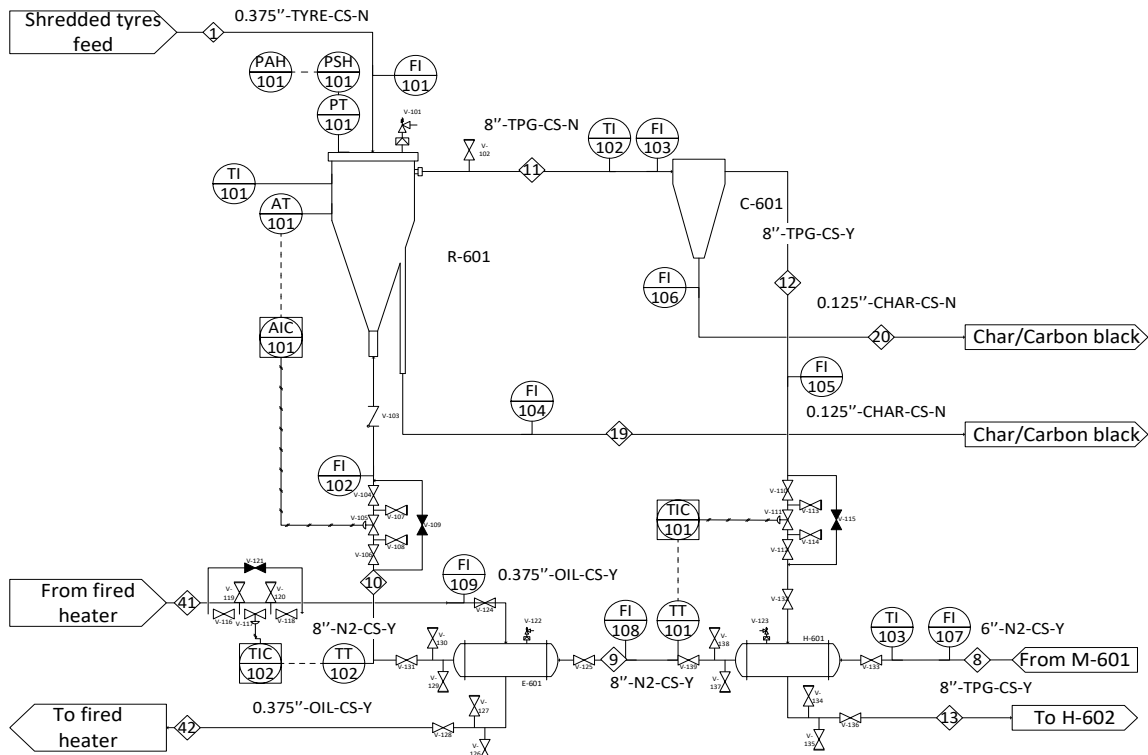


FIGURE 12. Piping and Instrumentation Diagram (P&ID) – Section 1

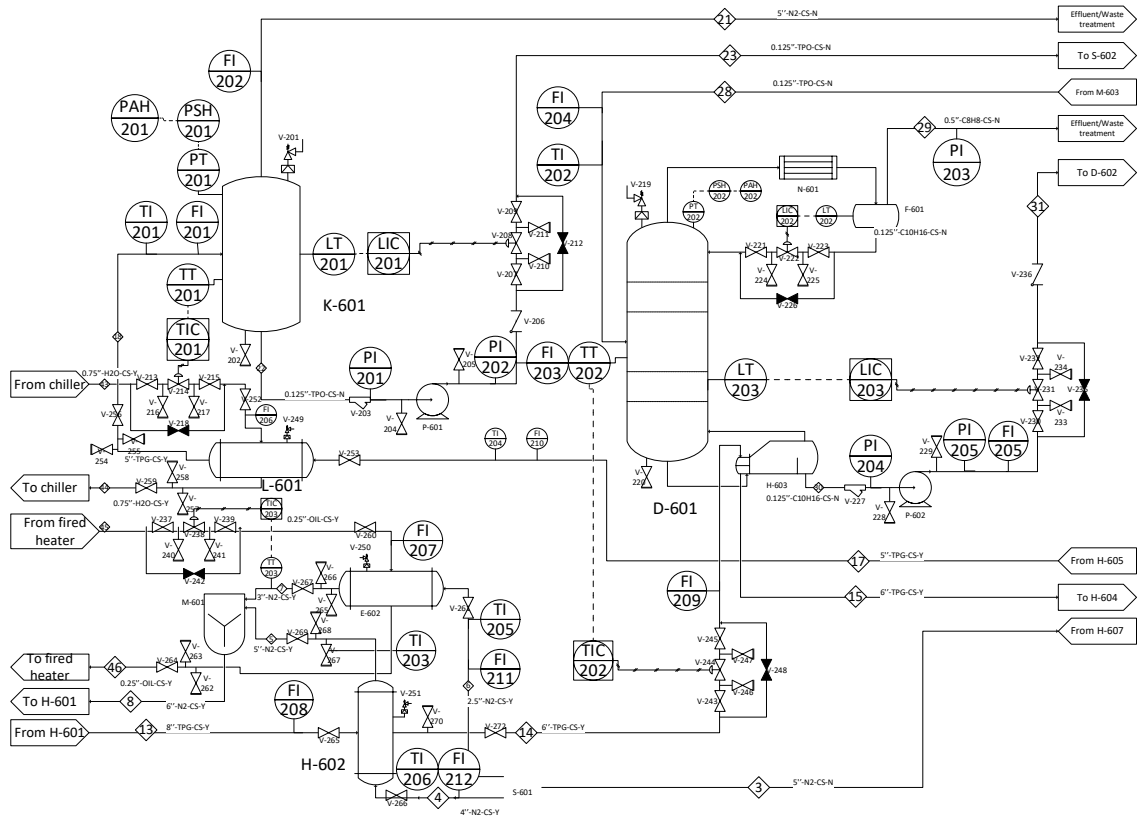


FIGURE 13. Piping and Instrumentation Diagram (P&ID) – Section 2

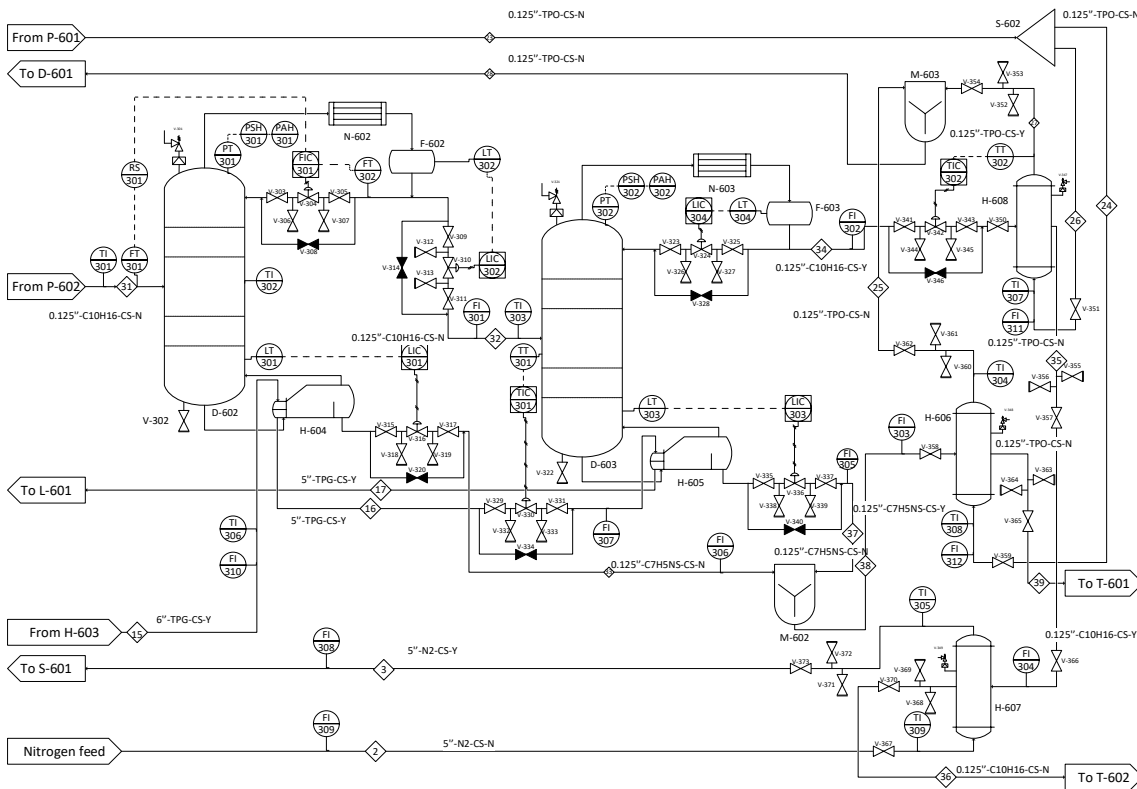


FIGURE 14. Piping and Instrumentation Diagram (P&ID) – Section 3



## PROJECT ECONOMIC EVALUATION

The total yearly profit of the pyrolysis operation relies on the principal product and by-products derived from the pyrolysis. The production of limonene (the primary product) will generate the majority of the revenue, while the sale of rubber pyrolytic oil and carbon black will generate additional revenue. The projected yearly revenue amount is displayed in Table 9.

The annual gross profit is projected by deducting the total annual production cost from the total yearly revenue produced. In the computation of the project's cash flow, the total amount invested in the capital (TCI) is divided into three periods, with 50% of TCI allocated to the first

year, 30% to the second, and 20% to the third. The TCI was calculated based on the fixed capital and working capital which including the equipment cost. It is a function of initial payments prior to the receipt of loan, and was calculated as 15% of the sum of Total Bare-Module (TBM) and total of Direct Permanent Investment (DPI). Alternatively, Method of Guthrie can be used for estimation of individual equipment cost (Lim et.al., 2020). In Year 4, the pyrolysis plant will begin operating at maximum capacity. As shown in Figure 15, a total project life span of 15 years is used for estimating the overall cash flow. With a simple payback time of 0.33 years, a return on investment of 303%, and a net present value of RM 432.2 million, the overall economic performance of the facility is positive.

TABLE 9. Calculation of the total annual revenue of the plant

Product Type	Component	Unit Price (RM/kg)	Annual Production Capacity (kg/year)	Annual Revenue (RM/year)	Reference
Main product	Limonene	243.00 {Sigma-Aldrich, #757}	543,089.05	131,970,639.15	Sigma-Aldrich (2023)
By-product	Tyre pyrolytic oil	6.53	199,201.46	1,300,785.53	Chemsain Konsultant. (2011)
By-product	Char/Carbon black	6.34	671,220.00	4,255,534.8	Qingdao Echemi Technology Co., Ltd. (2023)

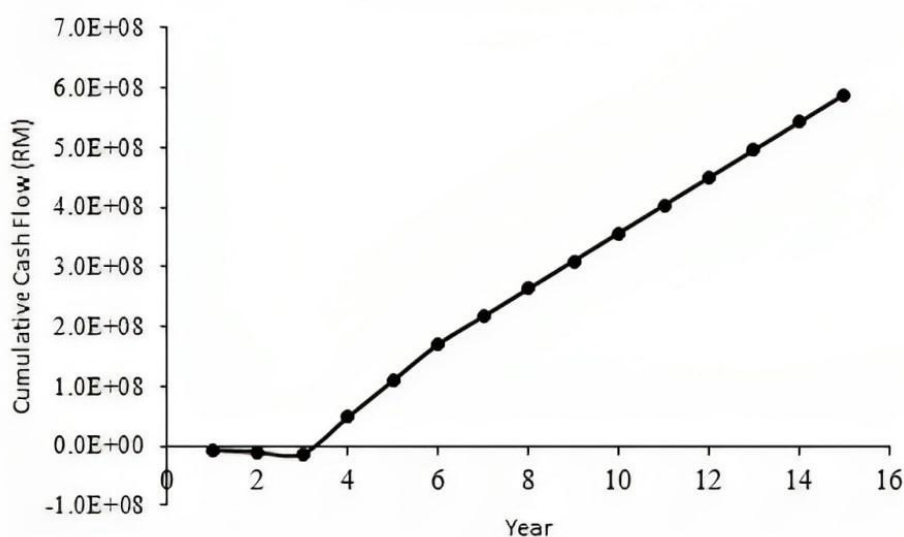


FIGURE 15. Cash flow diagram of the plant

## CONCLUSION

The goal of the present plant design project is to generate 543.1 tonnes yearly of limonene at a 98% purity level. In regard to five distinct levels, the Onion Model is utilised

for conceptual process development and synthesis. The handling of materials can be minimised and quality control can be enhanced with the continuous process operating mode. Through the PFD and P&ID, the input-output is then depicted with limonene as the primary product, tyre

pyrolytic oil (TPO) and char as by-products, and non-condensable gases as the waste. CSBR is chosen as the reactor design due to it is capable of handling viscous and irregular materials and permits intense gas-solid interaction that results in improved heat and mass transfer. The proposed operational temperature and pressure of the reactor are 425 °C and 1 atm, accordingly. The separation mechanism consists of a cyclone, a knock-out drum, and distillation towers which separate and purify limonene to a purity of 98%. Pinch analysis is performed for heat integration in order to minimise the total utility to 76.90 kW and save 78.68% of the energy. To assure product quality, process control and instrumentation are also proposed consisting of feedback and a feedforward PID control scheme. The controllers control the process parameters such as temperature, flow rate, liquid level, and composition in a CSBR, knock-out drum, distillation column, heat exchanger, and pump. By monitoring the perturbation variable and transmitting the signals to the ratio station, ratio PID control is also utilised. Finally, the plant cost and process economics are estimated by computing the capital expenditures and operating costs. The cash flow diagram for the undertaking reveals that it will break even in three years and three months. Additionally, the simple payback period, return on investment, and net present value have been estimated to be 0.33 years, 303%, and RM 432.2 million, accordingly, indicating that the project is lucrative, economically viable, and an achievable investment.

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#### DECLARATION OF COMPETING INTEREST

None

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