A techno- economic study of a fluidized bed vacuum reactor for mixed plastic pyrolysis.

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Background

- South Africa produces in excess of 500 000 tons p.a. of unrecyclable waste plastic (DST, 2014)

- Generally plastics cannot be easily recycled if they are constituted by **uncharacterized mixtures of different plastic types** or plastic-paper/metal combinations

- In this work we are developing and analyzing a catalytic pyrolysis technology that focuses on disposing of uncharacterized mixtures of different plastic types that is less impactful on landfill

Catalytic pyrolysis

- Pyrolysis is a thermal degradation process conducted in the absence of oxygen.

- Catalytic pyrolysis preferred over thermal (non-catalytic) pyrolysis as it produces a higher quality fuel oil at a lower temperature (from about 423 K), has faster reaction times and produces less volatile organic pollutants suggesting a less environmentally impactful process (Oh et al., 2018)

- Limitations include the energy cost to attain the pyrolysis temperature, catalyst cost and low catalyst reuse period depending on the reactor configuration.

- Optimization of catalytic pyrolysis involves selection of suitable inexpensive catalysts, catalyst regeneration, process variables and reactor type, condition and configuration optimization.

Literature

- Multiple reactor types have been reported on in literature at laboratory-scale and pilot-scale operations for the pyrolysis of waste plastic.

- The technology proposed in this work employs a unique lower pressure operation with a low-cost catalyst in a fluidized bed vacuum reactor (FBR).

- FBRs for catalytic cracking of plastic has been reported in the literature on the laboratory scale (0.42 kg/hr plastic pellets with reactor dimensions of 300 mm x 80mm ID) (Garforth et al., 1998; Lin et al., 2004; Lin and Yen, 2005; Liu et al., 1999; Marcilla et al., 2007; Mastral et al., 2001, 2006; Sharratt et al., 1997; Williams, 1998; Yan et al., 2005). However, research into the pyrolysis of mixed plastic waste using catalyst is limited.

- Advantages of FBR lies in the mixing which provides large surface area for the reaction to take place on the catalyst, higher efficiency of heat and mass transfer, high yield of pyrolysis oil (Gholizadeh et al., 2020), low capital and maintenance costs, and external heating makes the reactor body easier to clean and load (Al-Salem et al., 2017)

Methodology

- There are three parts/phases to the work presented. In the first phase, laboratory-scale vacuum pyrolysis experiments in a semi-batch reactor were conducted for mixed plastic waste to perform catalyst screening and process temperature and pressure optimization.
- The permutations considered for optimization include:
  - Catalyst (none, zeolite, zinc oxide)
  - Temperatures in the range of 450-821 K
  - Pressures from 30 kPa vacuum to 101 kPa absolute
- The compositions of the pyrolysis products were characterized by Gas Chromatography–Mass Spectrometry (GCMS) analysis. In the second phase, a pilot unit has been constructed and commissioned, with experimental conditions and design informed from the first phase. A series of experiments is ongoing to determine the operational limitations of the unit, char handling, emissions, product collection and testing. This will be presented in detail in future work.
- For the third phase of the project, a techno-economic analysis of a 100 $kg.hr^{-1}$ to-scale fluidized bed vacuum reactor was designed using simulation software (Aspen Plus ®) to determine if the proposed technology is cost-effective.

Experiments

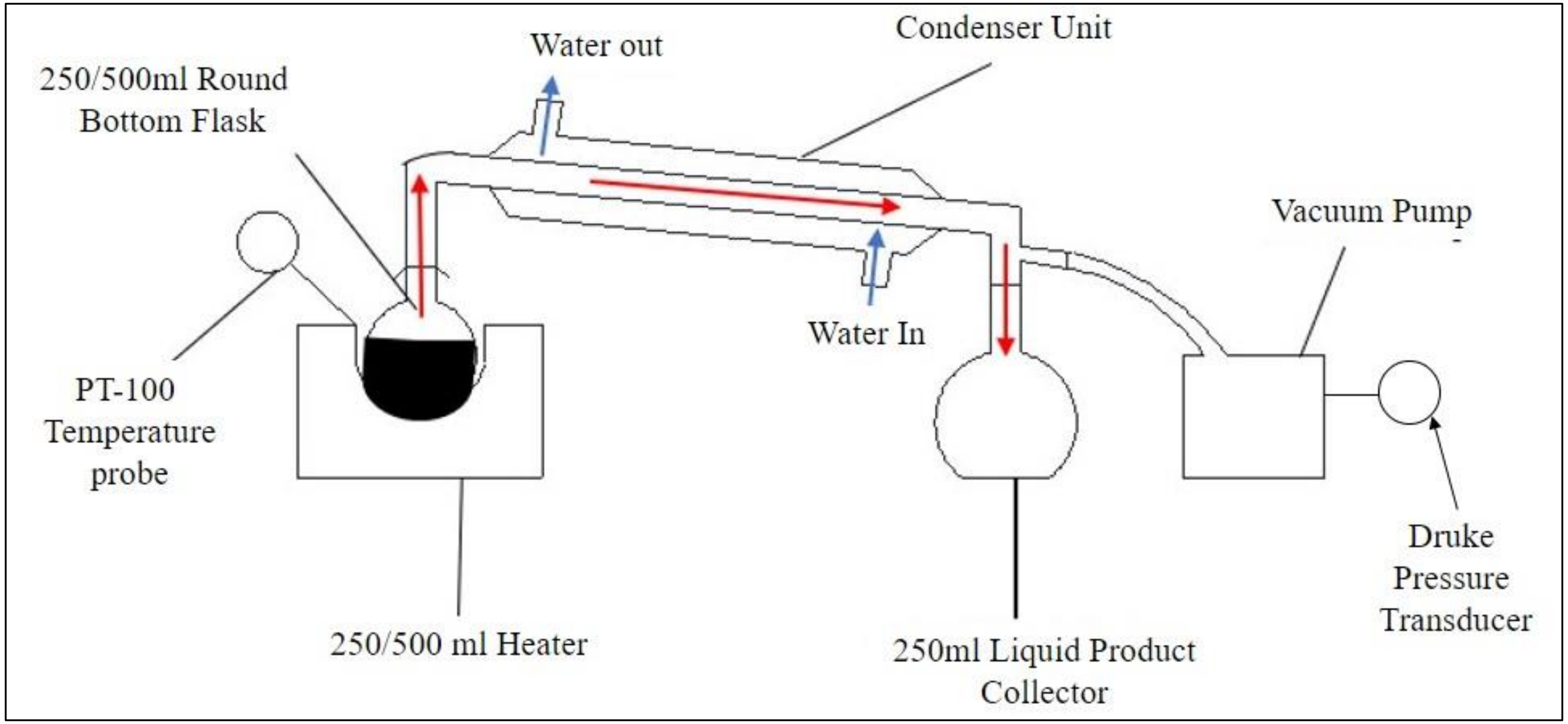
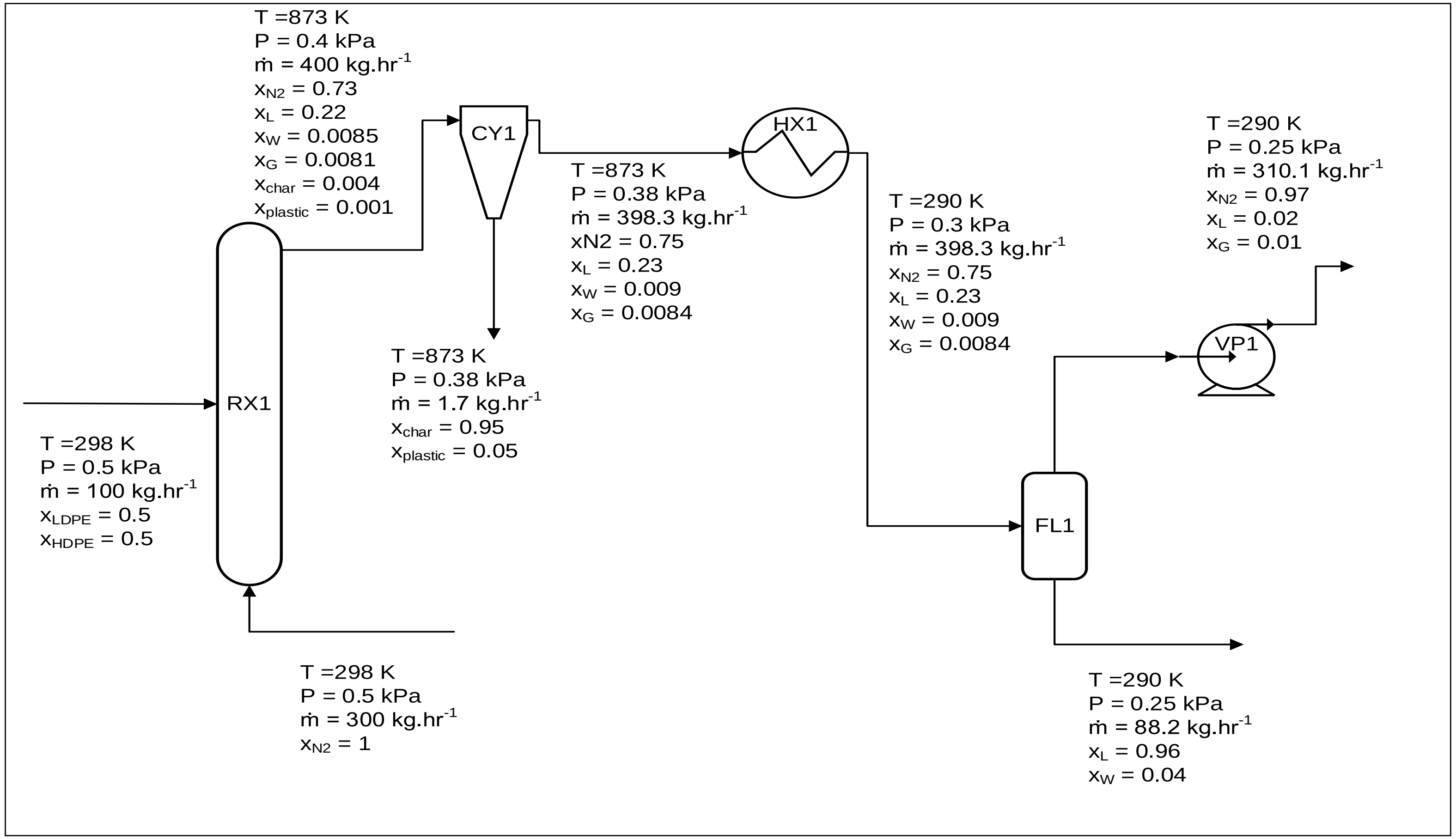


Figure 1: Experimental setup for lab-scale semi-batch pyrolysis measurements.

Model development



T =298 K
P = 0.5 kPa
$\dot{m}$ = 100 kg.hr^{-1}
x_{LDPE} = 0.5
x_{HDPE} = 0.5

T =298 K
P = 0.5 kPa
$\dot{m}$ = 300 kg.hr^{-1}
x_{N2} = 1

T =873 K
P = 0.4 kPa
$\dot{m}$ = 400 kg.hr^{-1}
x_{N2} = 0.73
x_L = 0.22
x_W = 0.0085
x_G = 0.0081
x_{char} = 0.004
$x_{plastic}$ = 0.001

T =873 K
P = 0.38 kPa
$\dot{m}$ = 1.7 kg.hr^{-1}
x_{char} = 0.95
$x_{plastic}$ = 0.05

T =873 K
P = 0.38 kPa
$\dot{m}$ = 398.3 kg.hr^{-1}
xN2 = 0.75
x_L = 0.23
x_W = 0.009
x_G = 0.0084

T =290 K
P = 0.3 kPa
$\dot{m}$ = 398.3 kg.hr^{-1}
x_{N2} = 0.75
x_L = 0.23
x_W = 0.009
x_G = 0.0084

T =290 K
P = 0.25 kPa
$\dot{m}$ = 310.1 kg.hr^{-1}
x_{N2} = 0.97
x_L = 0.02
x_G = 0.01

T =290 K
P = 0.25 kPa
$\dot{m}$ = 88.2 kg.hr^{-1}
x_L = 0.96
x_W = 0.04

Figure 2: Model of the proposed pyrolysis process with reactor run at 873 K.

T- temperature, P- pressure, $\dot{m}$- mass flow rate, x_i- mass fraction. RX1- Fluidized bed reaction, CY1- cyclone, HX1- Heat exchanger, FL1- Flash vessel, VP1- vacuum pump.

Results and Discussion

Table 1: Results of reaction yields by mass from lab-scale semi-batch experiments at approximately 40 kPa for LDPE and 1:1 LDPE to HDPE plastic feed.[a]

Run	Mass of plastic (g)	Mass of catalyst (g)	Duration (min)	Catalyst -to-feed Ratio	Pyrolysis Temp (K)	Conversion	Liquid		Char		Wax		Gas	
							Mass (g)	Yield[b] (%)	Mass (g)	Yield[b] (%)	Mass (g)	Yield[b] (%)	Mass (g)	Yield (%)
2	15.003	0.449	30	3:100	521	0.103	0.336	2.201	13.458	88.162	1.471	9.636	0	0
4	15.068	0.453	90	3:100	589	0.948	0	0	0.791	5.250	13.284	88.160	0.993	6.590
6	15.092	0.472	100	3:100	570	0.960	0.127	0.841	0.601	3.981	13.450	89.122	0.914	6.056
11	15.075	0.449	120	3:100	821	0. 962	11.203	74.315	0.325	2.156	1.160	7.695	2.387	15.834
12	15.055	0.447	100	3:100	818	0.966	11.575	76.887	0.435	2.889	1.379	9.162	1.665	11.062

[a] Run 1-6 feed: LDPE, Run 7-12 feed: 1:1 LDPE:HDPE, Uncertainties: u(P) = 2 kPa, u(m) = 0.002 g, u(t) = 2 min, u(T) = 2 K

[b] $yield\ \% = 100\frac{Change\ in\ product\ mass}{Initial\ plastic\ mass}$, gas yield calculated by difference

Table 2: Components reported in abundance in each product phase determined by GCMS analysis.

Product type	Degree of Abundance		
	1	2	3
Liquid	Pentadecane	Dec-1-ene	Heptadecane
Wax	Triacont-1-ene	Hentriacontane	Pentacosane
Gas	Oct-1-ene	Dodecane	Pentadecane

Results and Discussion

Table 3. Estimated kinetic data for the pyrolysis of mixed waste (1:1 LDPE/HDPE) estimated between 673-873 K.

Lumped component	k_0	E ($J.mol^{-1}$)
L	4.7	124300
W	40.6	26700
G	83.8	98900
C	121.1	44100

Where $k = k_0 e^{\frac{-E}{RT}}$ and R = 8.314 $J.mol^{-1}.K^{-1}$

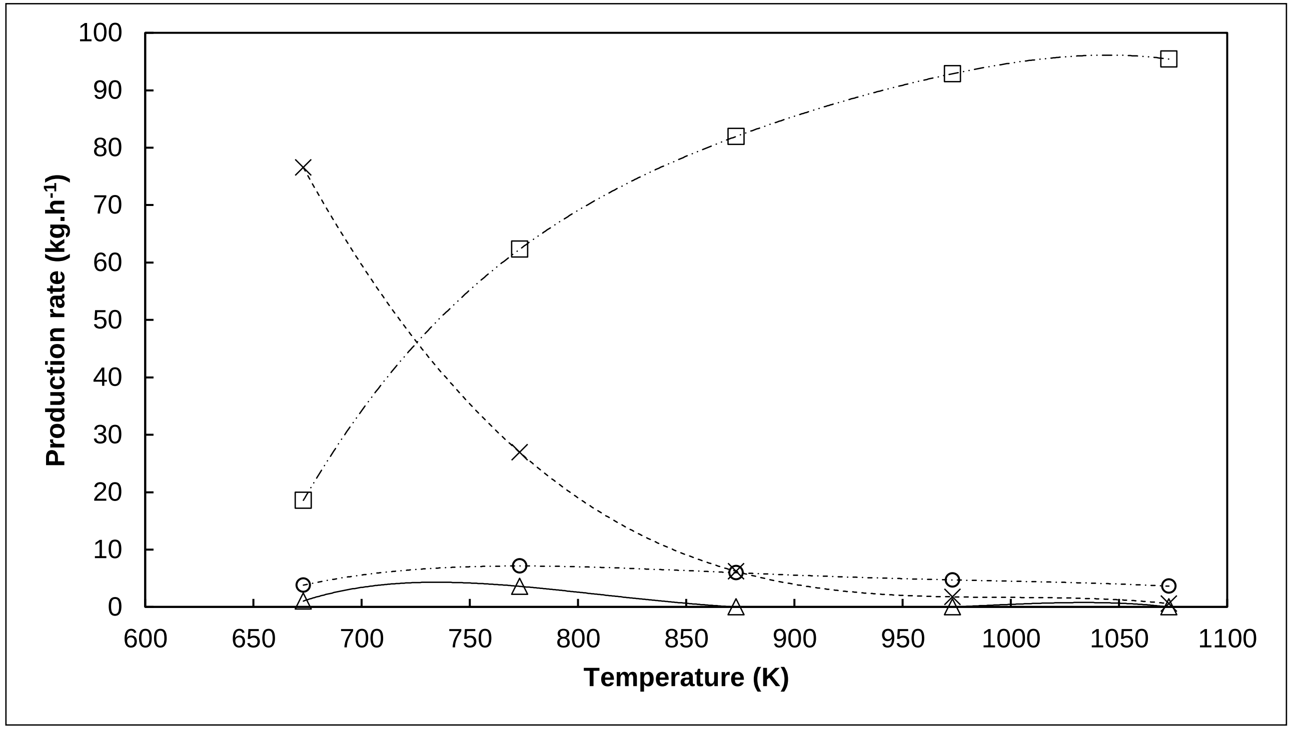


Figure 3: Effect of temperature on production rates of gas (○), liquid (□), wax (×) and char (Δ) for $100kg.hr^{-1}$ mixed waste plastic feed.

Preliminary cost model

Two scenarios for the liquid and wax fuel product selling prices were considered, i.e. (1) \$2.0/kg for liquid fuel and \$1.5/kg for wax, and (1) \$2.3/kg for liquid fuel and \$1.8/kg for wax and were determined based on profitability. These prices are competitive with global average prices of crude-based gasoline and wax.

Table 4: Proposed selling prices of pyrolysis products and the calculated MIRR.

Selling price of products	T (K)				
	MIRR (%)				
	673	773	873	973	1073
Selling price: liquid fuel (2\$/kg), wax (1.5/\$/kg)	15.9	19.2	19.7	19.9	20.3
Selling price: liquid fuel (2.30\$/kg), wax (1.80\$/kg)	17.5	20.3	20.8	20.9	21.3

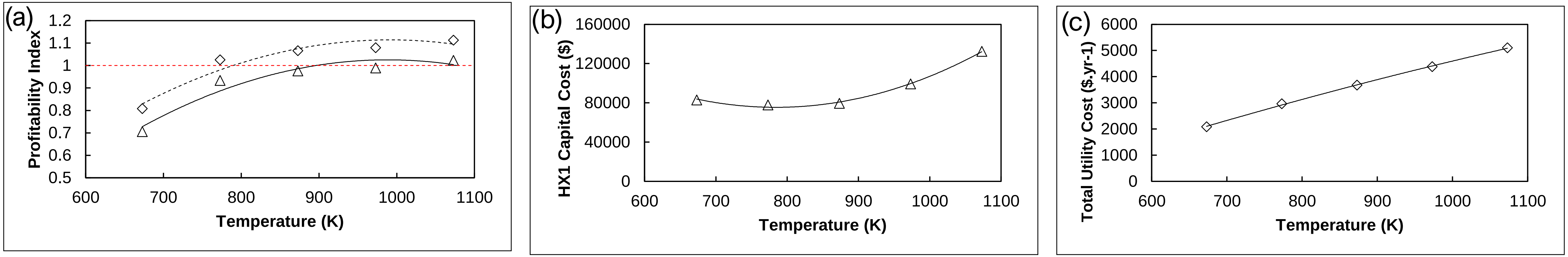


Figure 4: (a) Effect of reactor temperature on Profitability Index for two product prices, (b) Effect of reactor temperature on heat exchanger capital cost, (c) Effect of reactor temperature on process utility requirement.

Conclusions

- Mixed plastic (LDPE and HDPE) pyrolysis experiments were successfully conducted at the laboratory scale using zinc oxide catalyst.

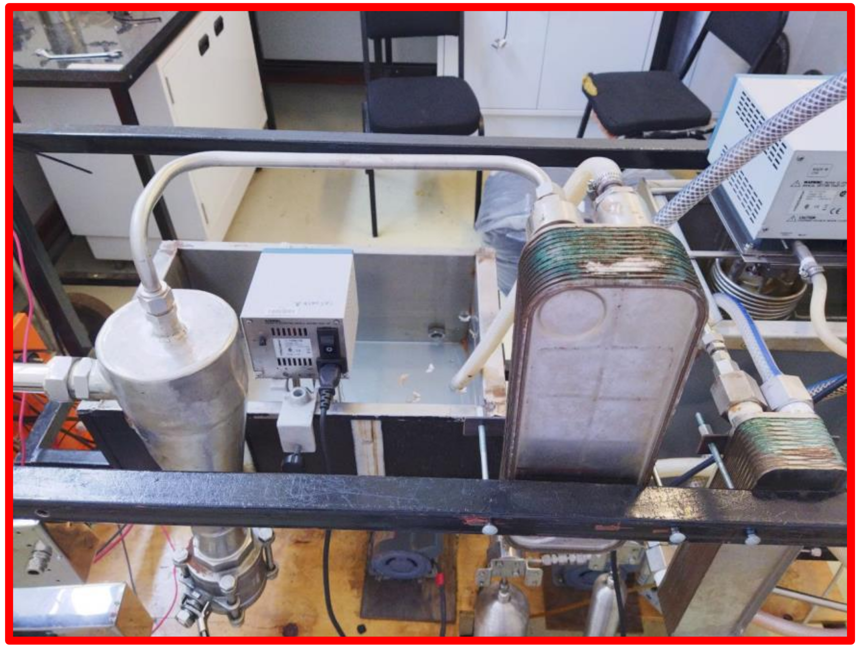
- High char yields were observed at temperatures below 610 K and high wax yields were observed below 670 K indicating that the more desired high liquid yields are only achievable at higher pyrolysis temperatures exceeding 700 K.

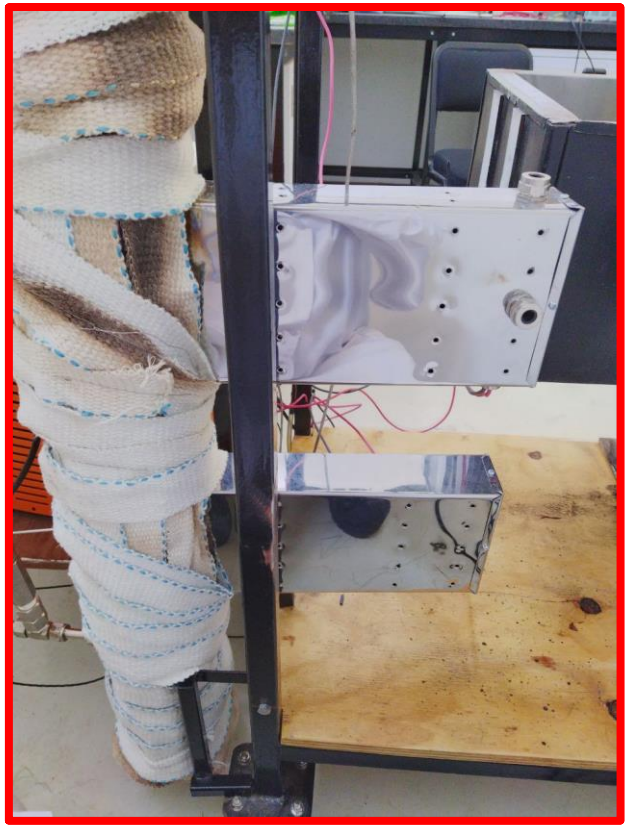
- The 100 kg.hr^{-1} mixed plastic pyrolysis process was successfully designed using Aspen Plus ® software.

- The preliminary lumped kinetic model successfully modelled the component class yields and replicated the effect of temperature on the reaction product cuts, as observed in the laboratory experimental study.

- A preliminary economic analysis was conducted using two different product price rates. It was found the proposed process can be profitable by running the reactor at 873 K, with a liquid fuel and wax selling price of 2.30$/kg and 1.80$/kg. This was indicated by a Profitability Index greater than 1 and a Modified Internal Rate of Return exceeding 20%.

Current and Future work





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