



Curtin University

Malaysia

Conversion of Palm Oil and Plastic Waste Mixtures for Hydrogen Enriched Syngas Production from Co-Gasification

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Speaker's Biography

Qualifications

- **Doctor of Philosophy in Chemical Engineering** (Thesis: Conversion of Polyethylene and Rubber Seed Shell Mixtures to Syngas using Ni Catalysed Steam Gasification Process), Universiti Teknologi PETRONAS (UTP), Malaysia.
- **Master of Philosophy in Mechanical Engineering** (Thesis: Studies of Syngas Cleaning Technologies Suitable for Power Generation from Biomass Oil Palm Shells), Curtin University Malaysia.
- **Bachelor of Chemical Engineering (Honours)**, Curtin University Malaysia

Research Interest

Bio-hydrogen production, Gasification, Pyrolysis, Syngas Cleaning Technologies, Green Technology

Website Profile



Google Scholar

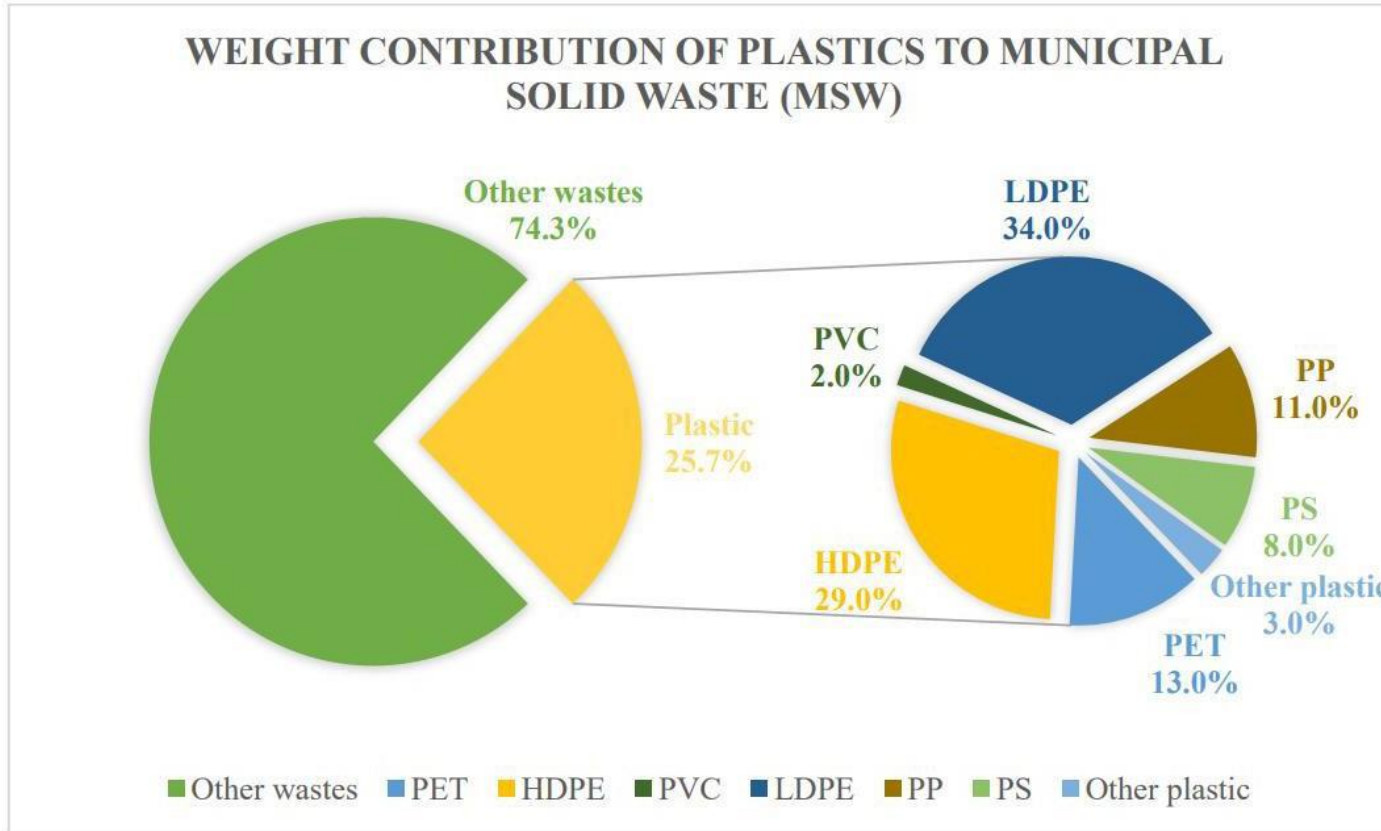


Presentation Outline

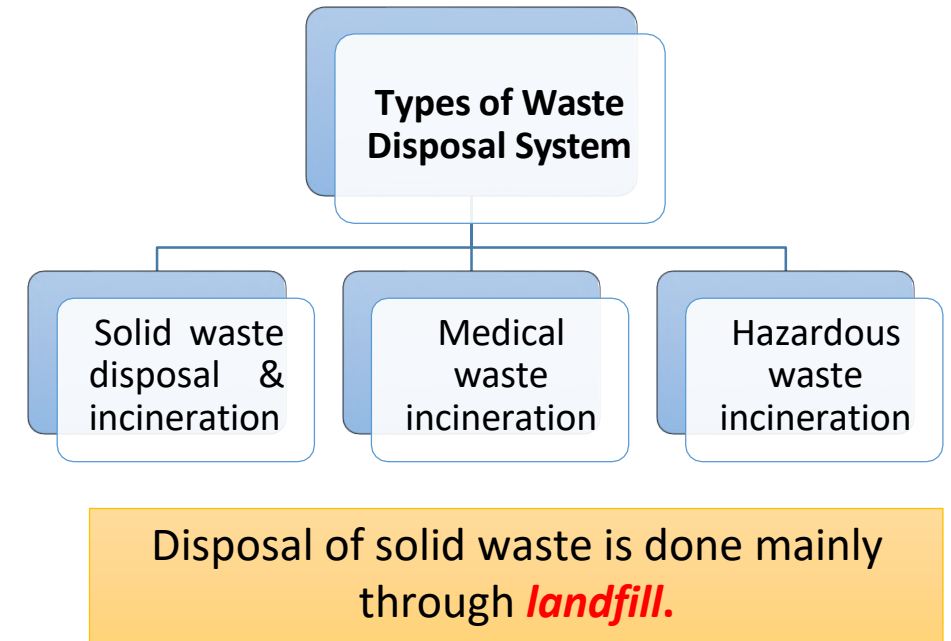
- Biomass and plastic as a source of fuel and properties
- Biomass and plastic conversion of fuel
- Thermochemical conversion of plastic and biomass waste mixtures
- Case study: Syngas production from palm kernel shell and polyethylene waste mixtures in fluidized bed steam co-gasification process




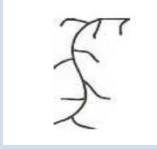
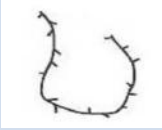
Research Background – Plastic Waste



Percentage of weight contribution of different plastic types to MSW (Aurpa, 2021)



Polyethylene Types

Polyethylene (PE) Type	LDPE	LLDPE	HDPE
Molecular Structure			
Degree of Branching per 1,000 C-atoms	High, 20-30 long and chain branches	Middle, 10-20 short chain branches up to 6 C-atoms	Low, 1-3 short chain branches from 1-2 C-atoms



Degree of branching reduce
(Easily to be broken down to smaller molecule)



Research Background – Palm based biomass

- Malaysia is presently in the second rank of the world's crude palm oil exporter next to Indonesia, with 24% of the total global crude palm oil production.

Activity	Biomass Waste	Quantity (%) of FFB in wet state
Oil palm plantation	Oil palm fronds	14.47 t ha ⁻¹
	Oil palm trunk	74.48 t ha ⁻¹
Palm oil milling	Empty fruit bunch (EFB)	22% of FFB
	Palm oil mill effluent (POME)	67% of FFB (0.65 M ³ t ⁻¹ FFB)
	Mesocarp fibre	13.5% of FFB
	Palm kernel shell	5.5% of FFB

Source: Hamzah et al., 2019 and Yeo et al., 2020

Calorific value of the palm based biomass

Biomass	Calorific Value (kJ/kg)
Empty Fruit Bunches	18,838
Shell	20,108
Fiber	19,068
Palm Kernel	18,900

Source: Shuit et al., 2009

Shuit et al., 2009. Oil palm biomass as a sustainable energy sources: a Malaysian case study. Energy (34), 1225-1235.

Hamzah et al., 2019. Solid fuel from oil palm biomass residues and municipal solid waste by hydrothermal treatment for electrical power generation in Malaysia: a review. Sustainability (11), 1060.

Yeo et al., 2020. Synthesis of sustainable circular economy in palm oil industry using graph-theoretical method. Sustainability (12), 8081.

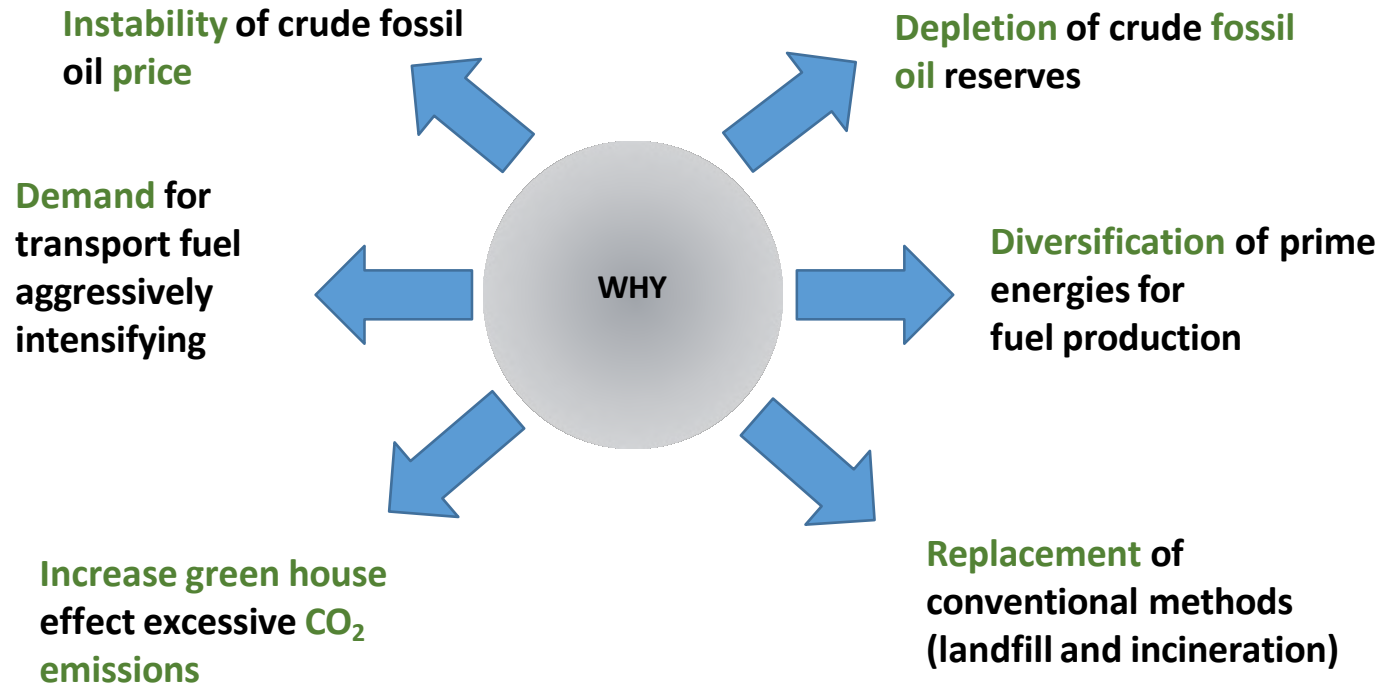


Motivation

Solution → *Co-Gasification of Plastic and Biomass Waste Mixtures*

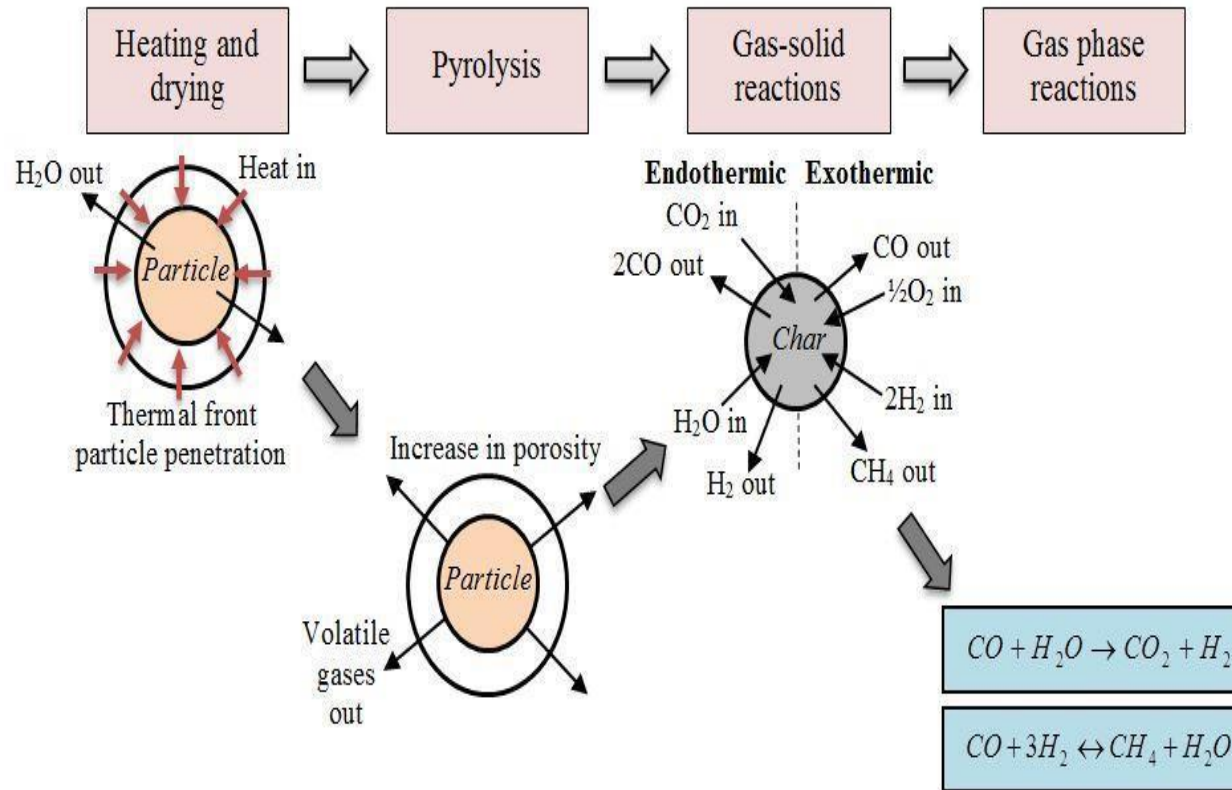
Gasification involves a set of complex thermochemical reactions that converts solid fuel to combustible gas using air/oxygen, steam or combinations of these oxidizing agents.

Why Gasification ?



Gasification

Gasification of solid waste involved four steps which are heating and drying, pyrolysis, gas-solid reaction, followed by gas phase reactions.



- Syngas is a fuel gas mixture of carbon monoxide (CO) and hydrogen (H₂).
- Can be upgraded into usable liquid and gaseous fuel such as synthetic natural fuel, lubricant, ammonia and dimethyl ether.
- Syngas can be produced through thermochemical conversion. Gasification of biomass is recognized as the most efficient way to convert biomass to gaseous product.

Synthesis Gas (Syngas)

Carbon
Monoxide
(CO)

Hydrogen
(H₂)



Desirable Syngas Quality for Different Application

	H ₂ /CO	CO ₂	Hydrocarbons	N ₂	H ₂ O	Contaminants Limit (ppm)
Fuel gas for turbine	Unimportant	Not critical	High	Unimportant	Unimportant	< 0.2 – 1.0 alkali metals
Fuel gas for boiler						< 1.2 alkali metals
Synthetic fuels	0.6	Low	Low	Low	Low	< 1.0 alkali metals
Methanol	~2.0	Unimportant	Low	Low	High	
Hydrogen	High	Unimportant	Low	Low	High	

Hydrogen costs used in long-term scenario for different processes

Method	Feedstock price	Feedstock cost (\$/GJ H ₂)	Other production cost (\$/G H ₂)	Transport cost (\$/GJ H ₂)	Refueling cost (\$/GJ/H ₂)	Total cost at fuel pump (\$/GJ H ₂)
Biomass gasification	2-5 \$/GJ	2.9-7.1	5-6	2-5	5-7	14-25
Coal with CCS	1-2 \$/GJ	1.3-2.7	4.7-6.3	2	5-7	13-18
Natural gas with CCS	3-4 \$/GJ	3.8-6.3	1.2-2.7	2	5-7	12-18
Offshore wind	4-5.5 cents/kWh	13.1-18.0	5	2-5	5-7	27-37
Solar Photovoltaic	12-20 cents/kWh	39.2-65.4	5	2-5	5-7	52-82
Onshore wind	3-4 cents/kWh	9.8-13.1	5	2-5	5-7	22-30
Solar thermal elec.	6-8 cents/kWh	19.6-26.1	5	2-5	5-7	32-42
Nuclear	2.3-3.5 cents/kWh	8.2-11.4	5	2	5-7	20-27



Energy Content of Various Fuels

Fuel	Energy Content (MJ/kg)
Hydrogen	120
Propane	49.6
Liquefied natural gas	54.4
Automotive gasoline	46.4
Aviation gasoline	46.8
Automotive gasoline	45.6
Methanol	19.7
Ethanol	29.6
Wood (Dry)	16.2
Coke	27.0
Bagasse	9.6

Dutta, S. 2014. A review on production, storage of hydrogen and its utilisation as an energy source. J. Ind. Eng. Chem. (20), 1148-1156.

Kalinci et al., 2009. Biomass-based hydrogen production : a review and analysis. Int. J. Hydrogen Energy (34), 8799-8817.

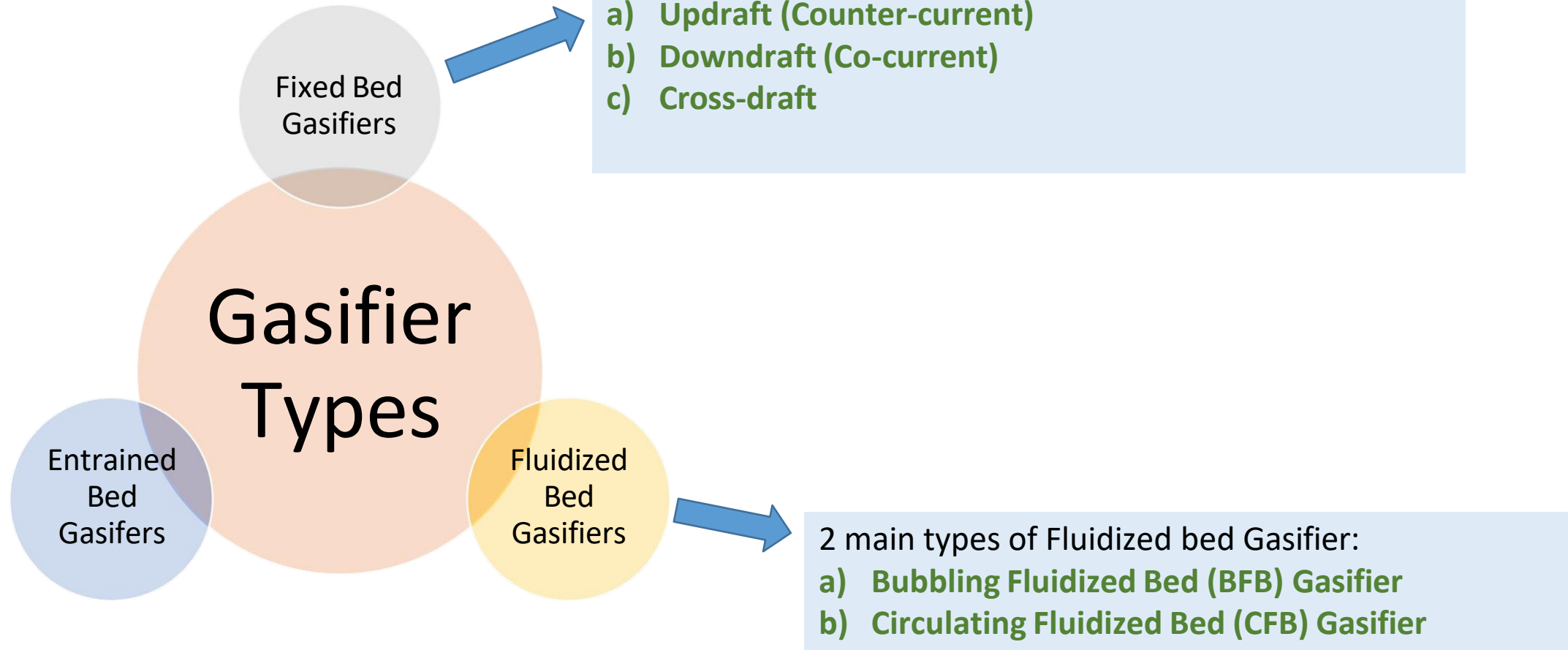


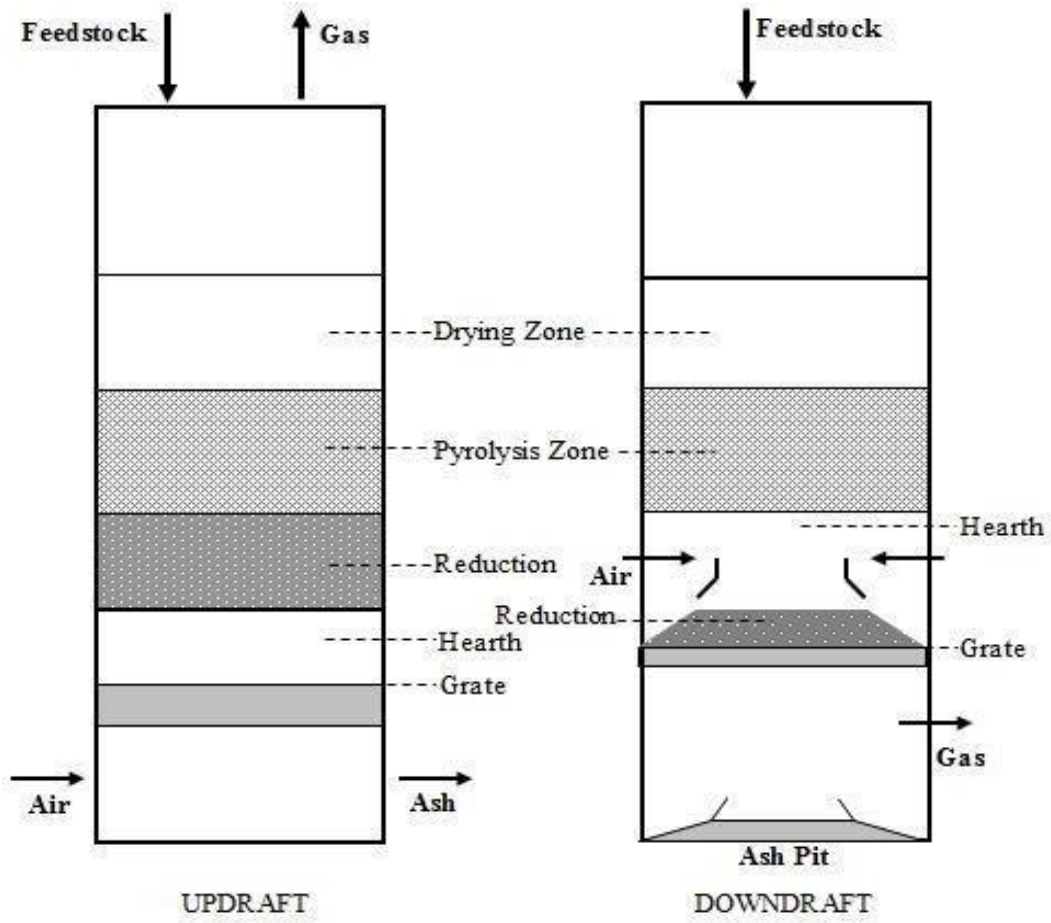
Classification of Gasification Processes

- **Mode of Gas-Solid Contacting (Gasifier Types)**
- **Gasification Agent:**
 - *Air gasification* produces a low heating value gas (**3.5-7 MJ/Nm³**)
 - *Pure oxygen gasification* provides higher heating value syngas (**10-12 MJ/Nm³**) in the absence of Nitrogen (N₂) gas
 - *Steam gasification* results in syngas with heating value of **10-15 MJ/Nm³**
 - *Hydrogen and steam* in a catalytic gasifier can produce a syngas with a very high heating value of **20-36 MJ/Nm³**
- **Heating of the Feedstock:**
 - In a **directly heated gasifier**, part of the fuel gets oxidized and the heat used.
 - **Indirect (or indirectly heated gasifier)** gasification
- **State of the Residue Removed:**
 - Slagging (ash is removed in liquid form) and
 - Non-slagging gasifiers (ash is removed in solid form).

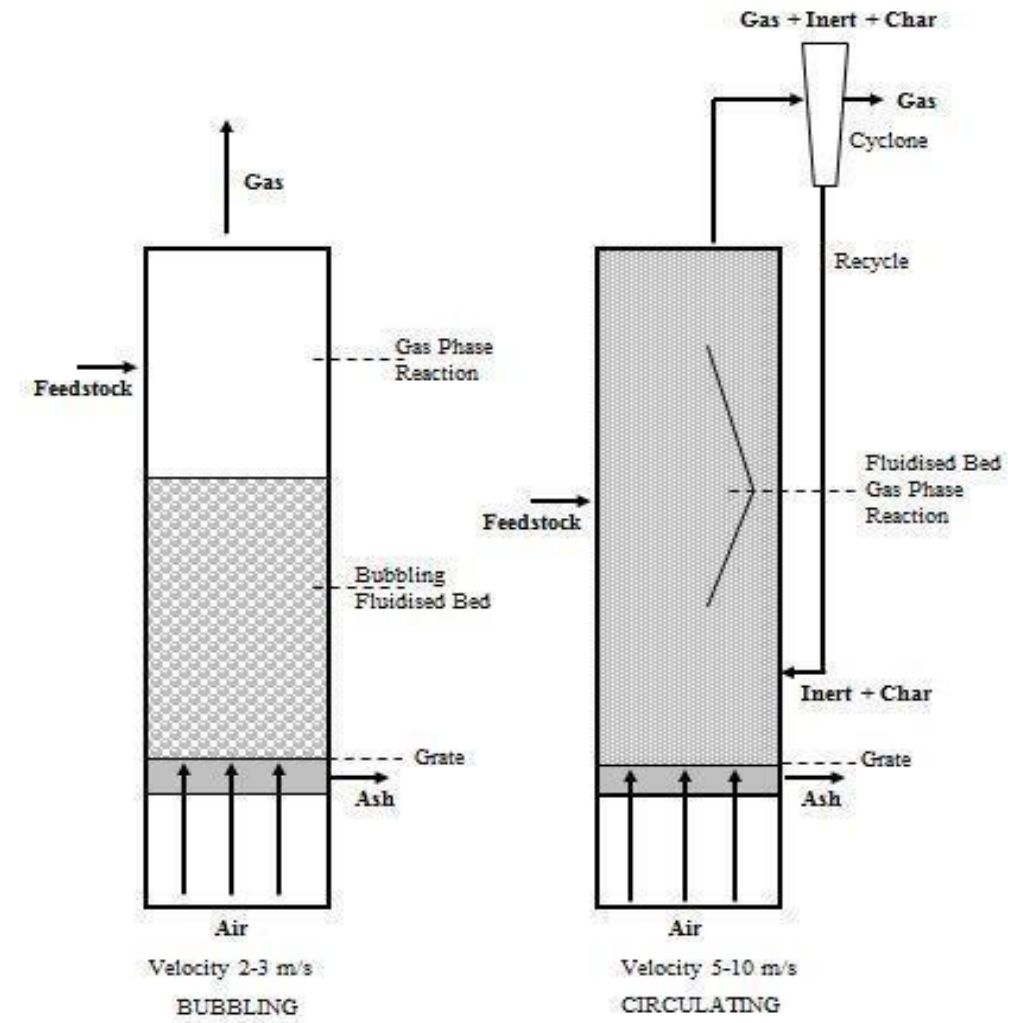


Gasifier Types





Fixed Bed Gasifier Configurations



Fluidised Bed Gasifier Configurations

Fixed Bed Gasifier Types

Updraft (Counter Current) Gasifier

Downdraft (Co Current) Gasifier

➤ **Major Advantages:**

- ▶ Easy to construct
- ▶ High char burnout
- ▶ Very good internal heat exchange, resulting in low temperatures
- ▶ Very high moisture can be tolerated (> 60% wet basis)
- ▶ Easy scale-up

Major Disadvantage:

- ▶ High amount of tar and other pyrolysis products are drawn out with the product gas. Hence, producer gas has a high tar content.

➤ **Major Advantage:**

- ▶ Low tar content in producer gas

Major Disadvantages:

- ▶ High amounts of ash and dust particles remain in the gas since the gas will have to pass through the combustion or reduction zones.
- ▶ High exit temperature (~700°C) since heat exchange of the producer gas with the feedstock in the drying zone does not take place here.
- ▶ Difficult to scale up
- ▶ Fuel requirements are strict. Particle size (1-30 cm), maximum moisture content of 25%, fines particles are not suitable as will attribute to throat blockages.

Fluidised Bed Gasifier

➤ Major Advantages:

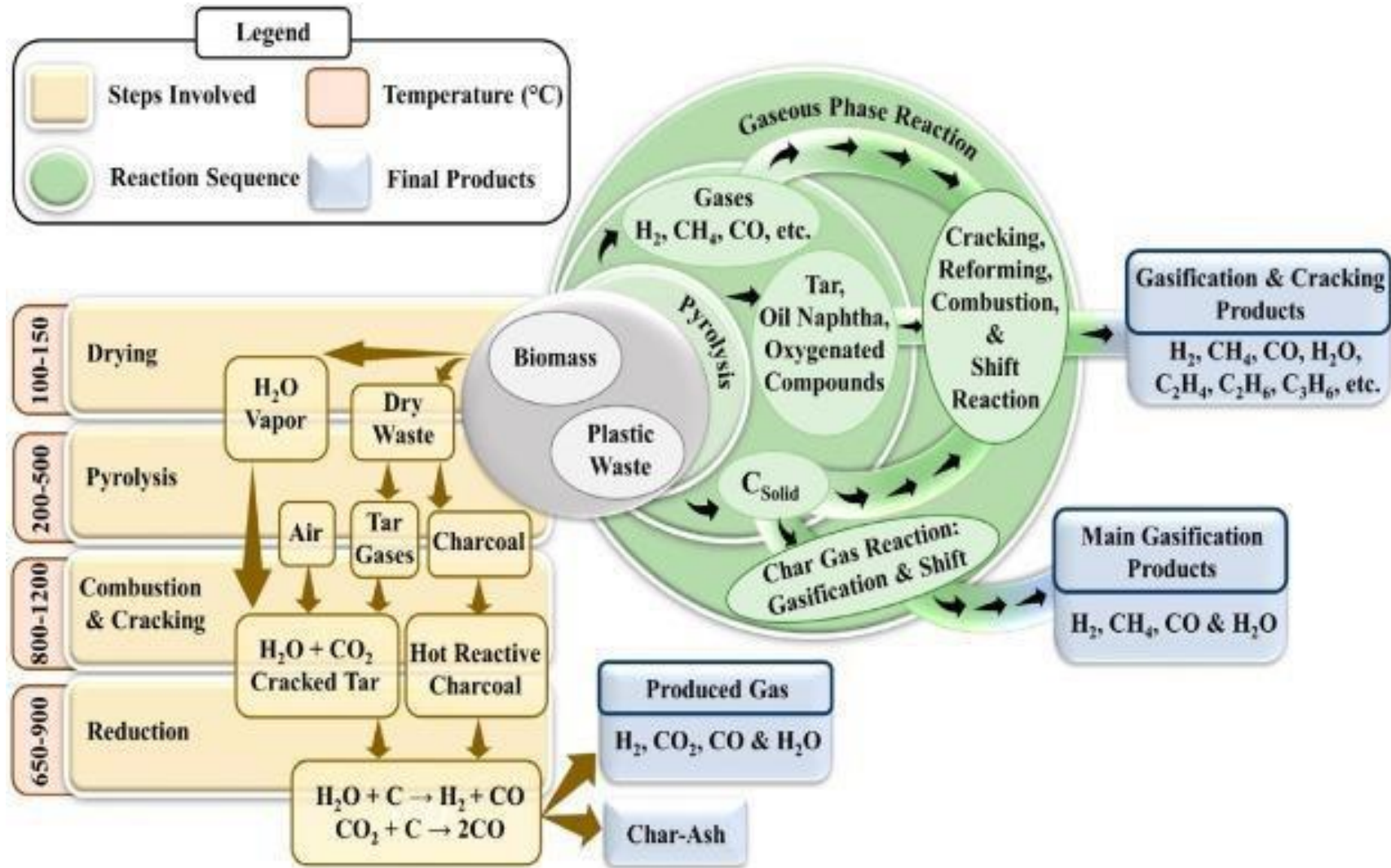
- ▶ Can offer high throughput capabilities
- ▶ Greater fuel flexibility including handle low-density feedstock

Major Disadvantage:

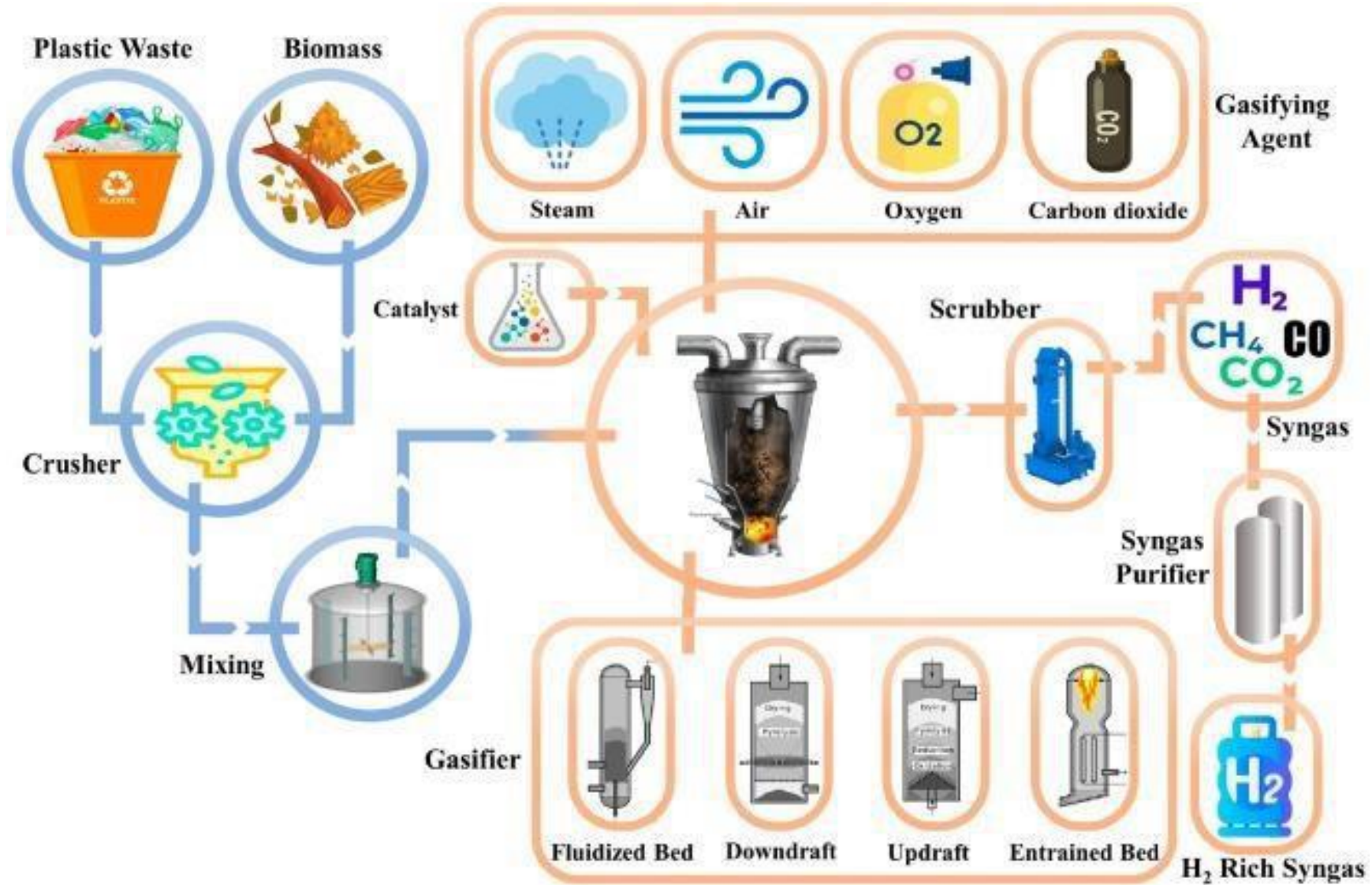
- ▶ Gas quality is difficult to be controlled resulting in conflict between high reactions temperature.
- ▶ More particulate carryover in a fluidized bed gasifier.



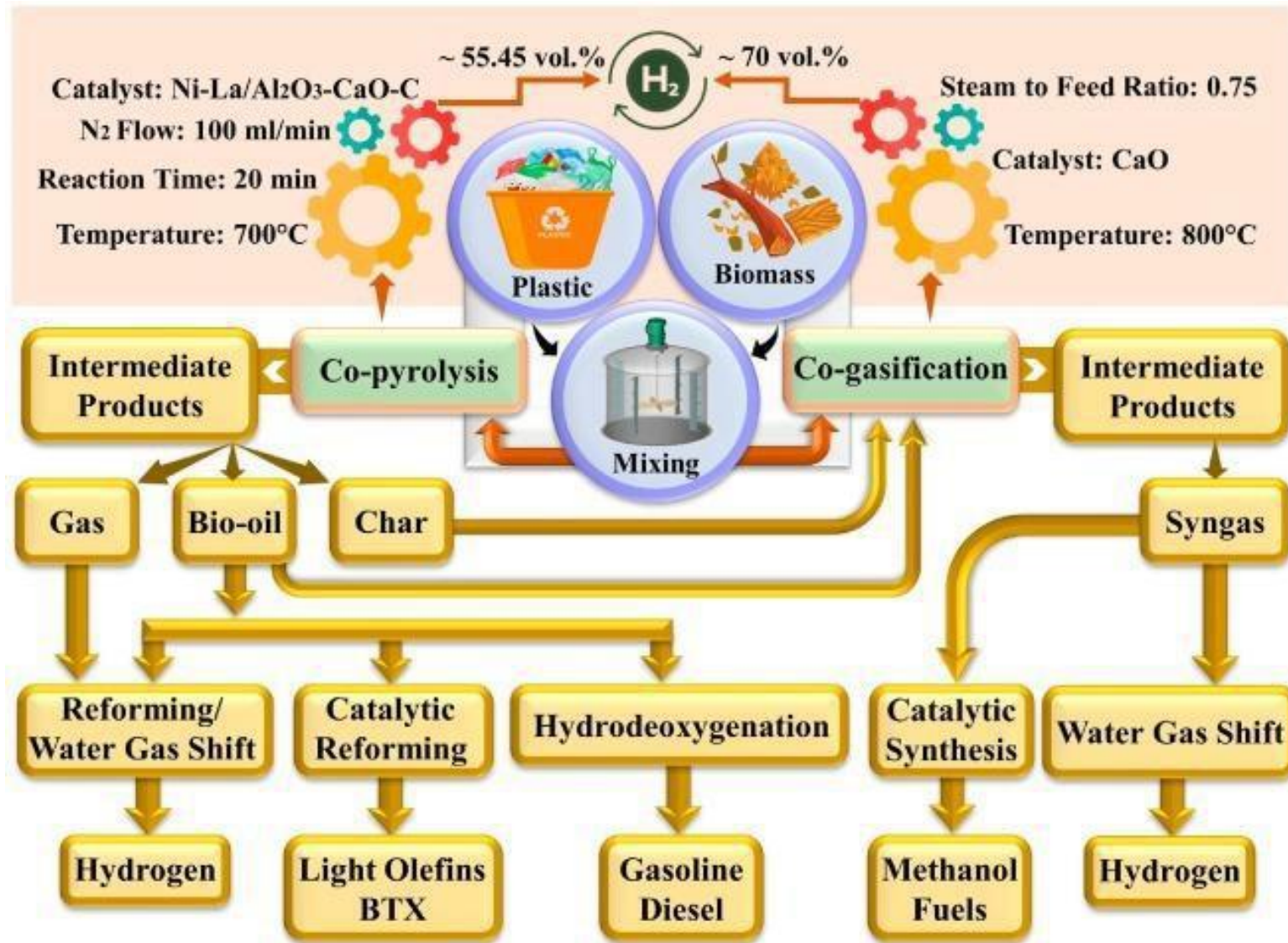
Steps Involved and Reaction Sequence of Co-Gasification for Biomass and Plastic Waste Mixtures



Schematic Diagram of Biomass and Plastic Waste Co-Gasification to Produce Hydrogen Gas



Comparison and Schematic Representation of Co-Pyrolysis and Co-Gasification Process



Hydrogen production using co-gasification of biomass and plastic waste mixtures

Biomass	Plastic	Catalyst	Temperature (°C)	H ₂ production	Other key findings	Ref.
Poplar wood chips	Polyethylene (PE)	-	286-985	17.64%	-H ₂ and CO increased in the produced gas by injecting steam	Harouna et al. (2020)
Palm kernel shell (PKS)	Polystyrene (PS)	-	700-900	5.6-13.1 vol%	-Higher gas concentration by increasing PS at 900°C	Basha et al. (2020)
Beech wood	PE	ZSM-5	~850	7.92 mol/h	-H ₂ content in syngas was affected by feedstock composition. -Higher production of H ₂ with a smaller biomass-to-PE ratio.	Lun et al. (2019)
Coconut shell (CS)	High density polyethylene (HDPE)	Ni	600-800	49.76-81.6 vol%	- Increase in syngas and H ₂ due to the presence of Ni catalyst, which enhances HDPE/CS ratio. - Gasifier temperature affects the produced gas.	Esfahani et al. (2017)
Pine	HDPE	Ni	500-700	65.27-72 vol%	-Gaseous stream and H ₂ increased with a higher HDPE content in the mixture. -Deactivation of the catalyst is affected in the reforming step by feedstock composition.	Arregi et al. (2017)
Wood	Polyethylene terephthalate (PET)	Synthetic olivine	725, 800, 875	4.3-5.4 vol%	-Production of coke is prevented above the bed by wood and PET contact	Robinson et al. (2016)



Number of studies reported on thermochemical conversion technologies in Malaysia

Feedstock	Thermochemical Conversion Technologies			
	Gasification	Pyrolysis	Liquefaction	Hydro processing
EFB	4	2	4	
OPF	1		1	
PKS	5		300	
Polyethylene	1			
Coconut shell	1			
FPF			3	
PKS-derived bio-oil				1
Phenol, cresol, guaiacol				4
Waste cooking oil				1
Jatropha oil				1
Palm oil				1
Wood pellets		2		
Rubberwood		1		
Microalgae		1		
Rice Husk		1		



Case Study:

Syngas production from palm kernel shell and polyethylene waste mixtures via catalytic steam co-gasification process

Energy 75 (2014) 40–44

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Syngas production from palm kernel shell and polyethylene waste blend in fluidized bed catalytic steam co-gasification process

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ABSTRACT

Energy from renewable source is expected to complement the energy derived from fossil fuel resources. Gasification is a versatile thermochemical process for solid waste fuel conversion. In the current paper, syngas production from palm kernel shell (PKS) and polyethylene waste blend in a catalytic steam gasification process is studied. In order to acquire the optimum condition of syngas production, the effect of main variables such as reaction temperature, steam/feedstock (S/F) ratio, polyethylene waste/biomass (P/B) ratio on syngas production was investigated and optimized via Taguchi design of experiment approach. Under the optimized condition of 800 °C, P/B ratio: 0.3 w/w and S/F ratio: 1 w/w, the total syngas yield and hydrogen yield achieved are 422.40 g syngas/kg feedstock and 135.27 g H₂/kg feedstock, respectively.

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Feedstock Characterisation

Proximate Analysis

Proximate analysis (wt%, wet basis)	Palm Kernel Shell (PKS)	High Density Polyethylene (HDPE)
Moisture content	12.00	0.00
Volatile matter	30.53	99.67
Fixed carbon	48.50	0.00
Ash	8.97	0.33

Ultimate Analysis

Ultimate analysis (wt%, dry basis)	Palm Kernel Shell (PKS)	High Density Polyethylene (HDPE)
Carbon	49.23	85.71
Hydrogen	5.03	14.29
Oxygen	44.94	0.00
Nitrogen	0.74	0.00
Sulphur	0.05	0.00



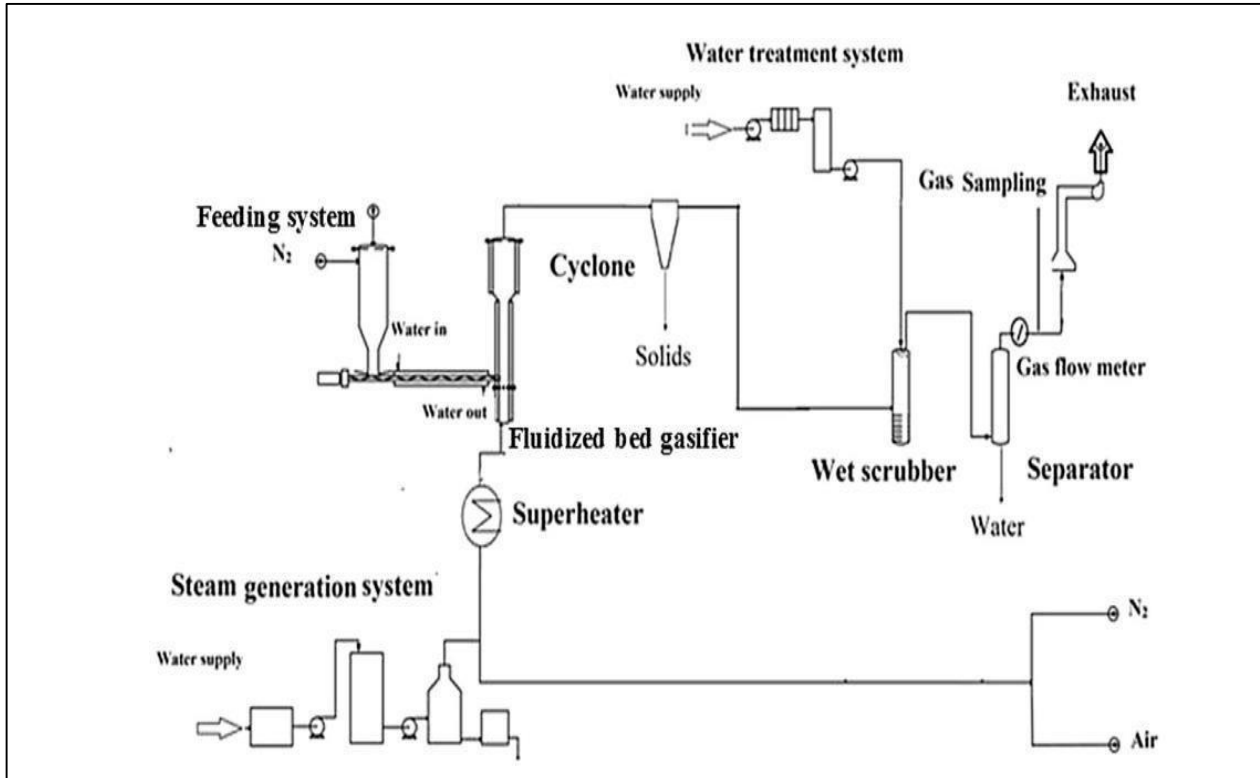
Catalyst Characterisation

Dolomite

Chemical Components	Formula	Value
Calcium oxide	CaO	32.00% min
Calcium carbonate	CaCO ₃	60.00% min
Magnesium oxide	MgO	16.00% min
Magnesium carbonate	MgCO ₃	34.00% min
Iron oxide	Fe ₂ O ₃	2.00% min
Aluminum oxide	Al ₂ O ₃	2.00% max
Silicon dioxide - Silica	SiO ₂	2.00% max
Moisture		2.00% max
Bulk density (kg/m ³)		1,100-1,300



Experimental Procedures



Process flow diagram of pilot plant catalytic steam gasification system

Pilot Plant Fluidised Bed Gasifier Description

1. Pilot unit consists of 2 cylindrical reactors made of Inconel 625.
2. Fluidised bed gasifier dimension (H: 2,500 mm; internal diameter: 150 mm (gasification zone), and 200 mm (free board zone))
3. Fixed bed gasifier dimension (H: 2,500 mm; internal diameter: 150 mm)
4. Gasifiers equipped with 4 individual electrical heaters and 8 thermocouples for controlling temperature profile across each reactor)

Process Parameters

Feeding Rate = 2 kg/hr

Catalyst Used: Dolomite

Process Parameters Involved:

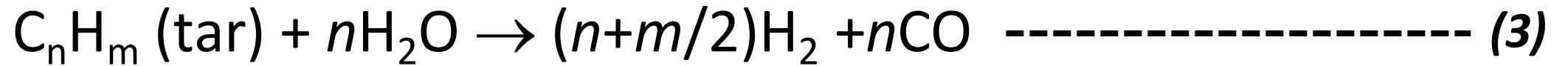
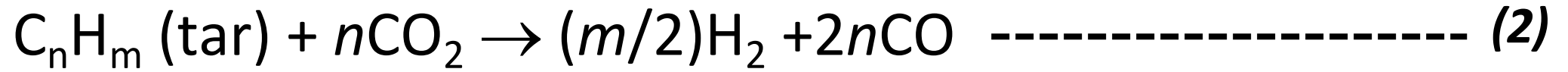
Reaction Temperature = 650-800°C

Steam to Feedstock Ratio (S/F) = 1-3

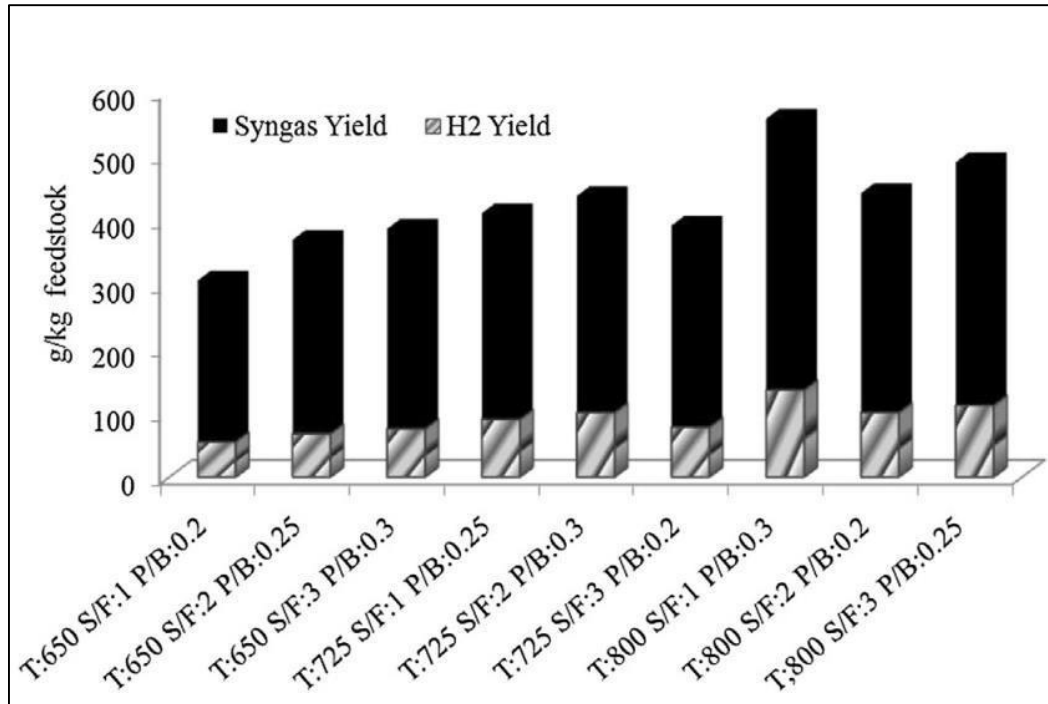
Polyethylene to Biomass Ratio = 0.2-0.3



Reactions Involved during the Co-Gasification of PE and PKS mixtures with the presence of dolomite catalyst (in fixed reactor)



1. Effect of Temperature

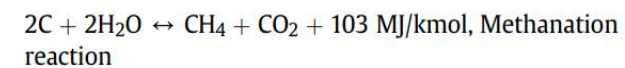
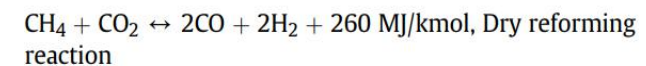
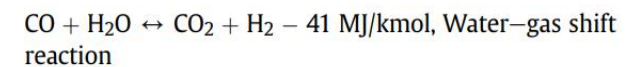
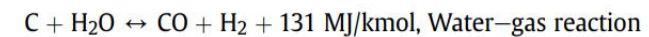
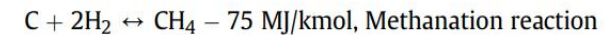
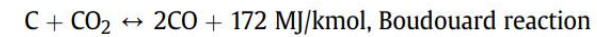
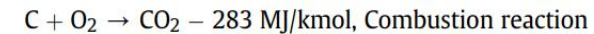


Effect of variables on product yield

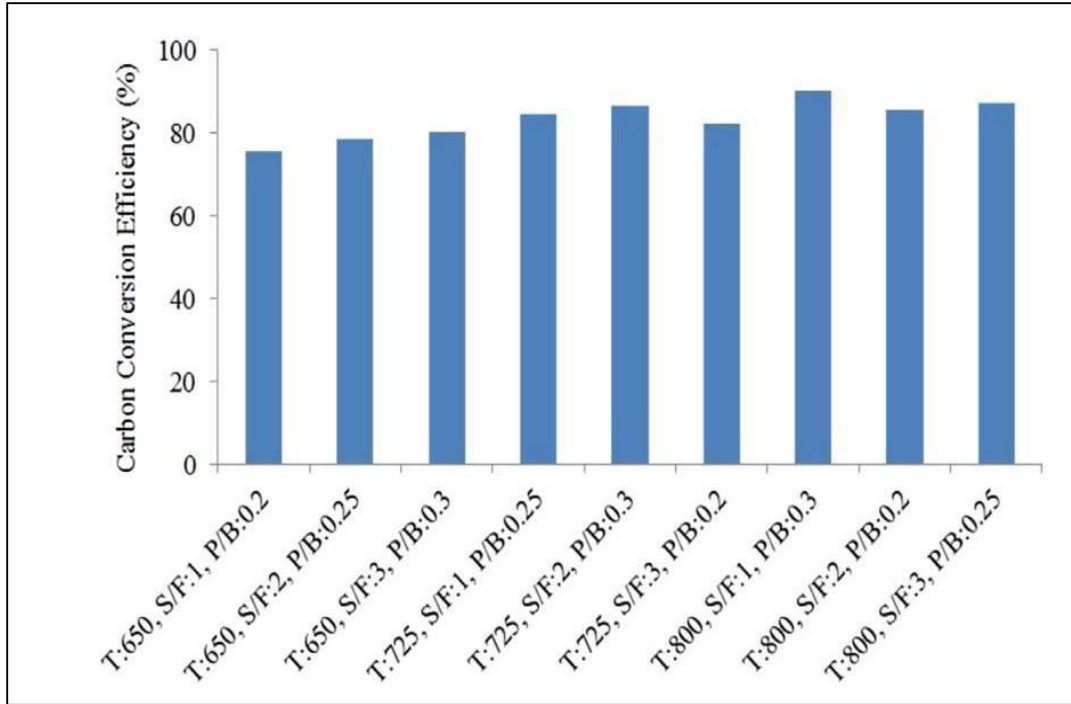
T: Temperature (°C), S/F: Steam to Biomass Ratio (w/w), P/B: Polyethylene to Biomass Ratio (w/w)

- Temperature exhibits most crucial effect on catalytic steam gasification and has major influence on final product composition.
- High temperature enhances syngas production yield due to (i) water-gas shift reaction, (ii) steam methane reforming, and (iii) dry reforming reaction.

Principal Reactions taking place in gasification process:



2. Effect of Steam/Feedstock (S/F)



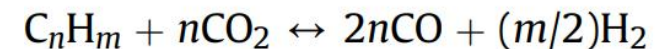
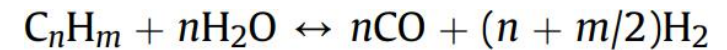
Effect of variables on carbon conversion efficiency (CCE)

T: Temperature (°C), S/F: Steam to Biomass Ratio (w/w), P/B: Polyethylene to Biomass Ratio (w/w)

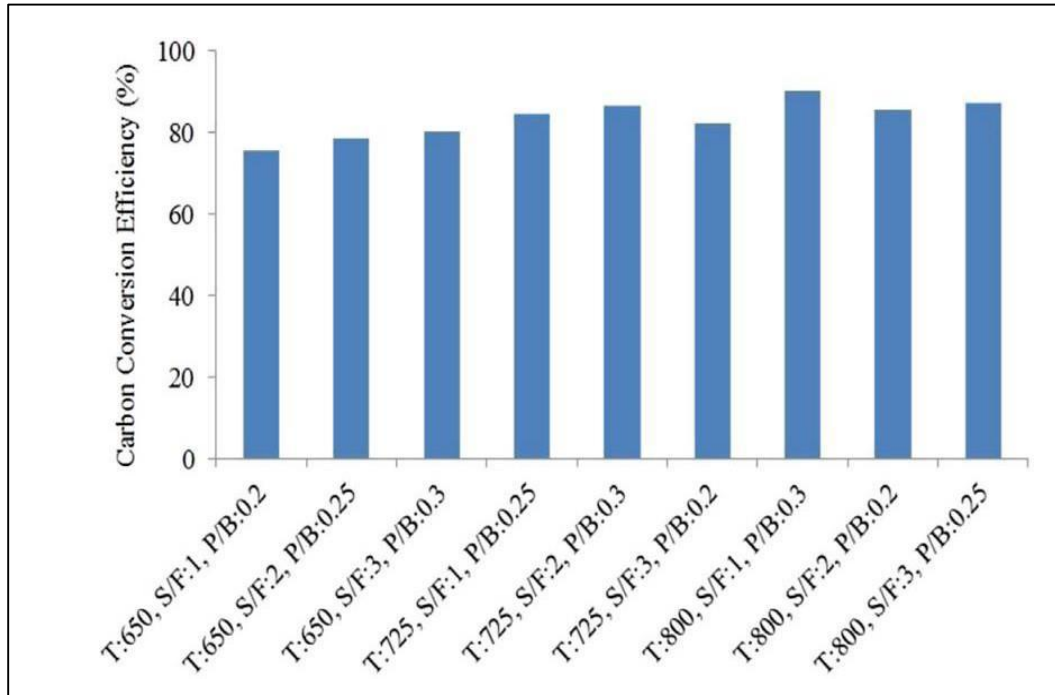
- Gasification efficiency was reflected by the CCE which is 90.2% and was calculated by the following Equation:

$$X_C (\%) = (12(\text{CO}\% + \text{CO}_2\% + \text{CH}_4\% + 2 * \text{C}_2\text{H}_4\%)/(22.4 * \text{C}\%)) * 100(15)$$

- By increasing temperature from 650 to 800 °C and constant P/B ratio, max. syngas (**341.08 g syngas/kg feedstock**) and H₂ yield (**100.43 g H₂/kg**) achieved at 800°C.
- Increasing temperature leads favors products formation for endothermic reaction (accordance to Le Chatelier's principle).
- Reforming equations shown below becomes more dominant and cause syngas composition to increase and decrease of hydrocarbons and CO₂ content.



2. Effect of Steam/Feedstock (S/F)



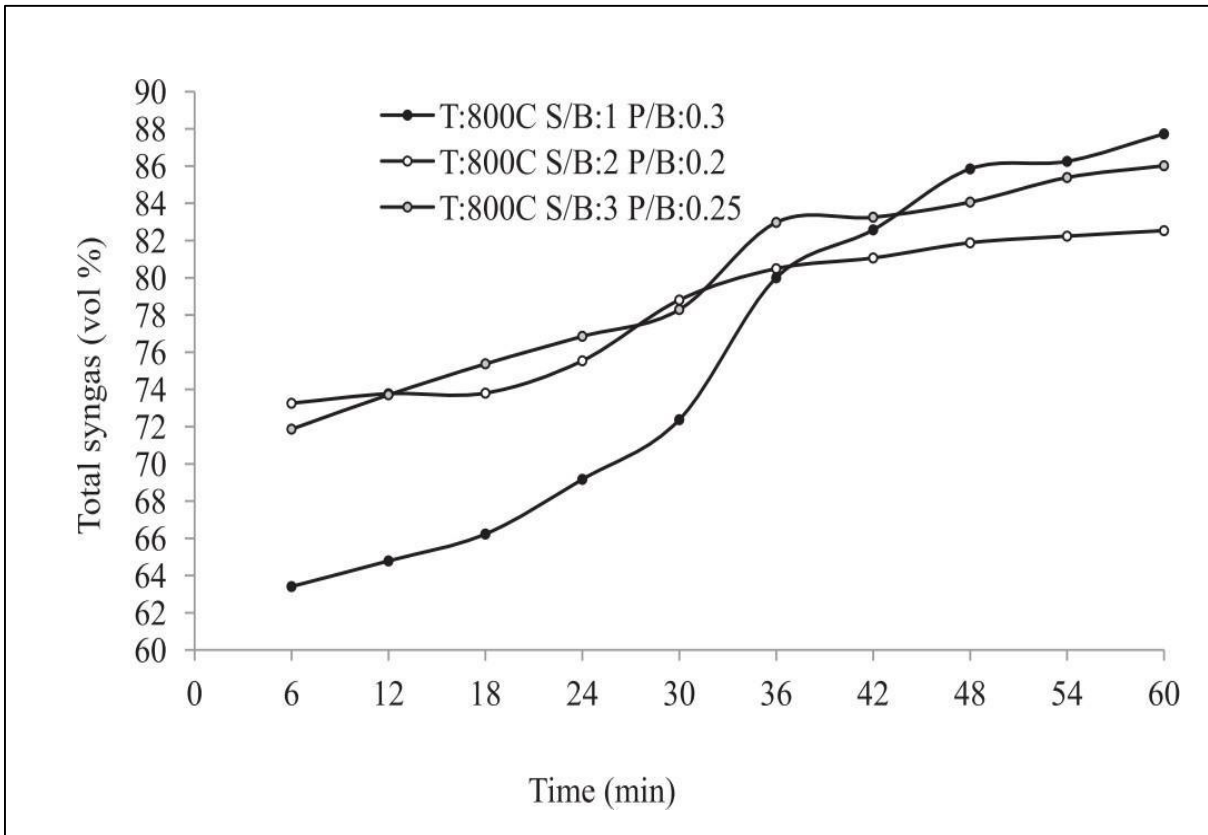
Effect of variables on carbon conversion efficiency (CCE)

T: Temperature (°C), S/F: Steam to Biomass Ratio (w/w), P/B: Polyethylene to Biomass Ratio (w/w)

- S/F ratio is an influential parameter on the gasification process.
- By applying steam as the gasifying agent, both methane and reforming and water-gas shift reactions are becoming dominant as the main conversion reactions in catalytic gasification process and will enhance the syngas production.
- As S/F ratio increased from 2 to 3 w/w (at 800°C), the dry reforming **syngas yield increased** from **341.08 to 422.40 syngas/kg feedstock** and **H₂ yield increased** from **100.43 to 135.27 g H₂/kg feedstock**.
- By increasing S/F ratio from 2 to 3 w/w at temperature of 725 °C, **syngas yield decreased** from **336.82 g syngas/kg feedstock** to **313.45 g syngas/kg feedstock**. Introducing excess steam to gasification process will increase hydrocarbon cracking. However, excessive steam would lower gasification temperature >>Syngas quality degrades.



3. Effect of Polyethylene Waste Blending Ratio

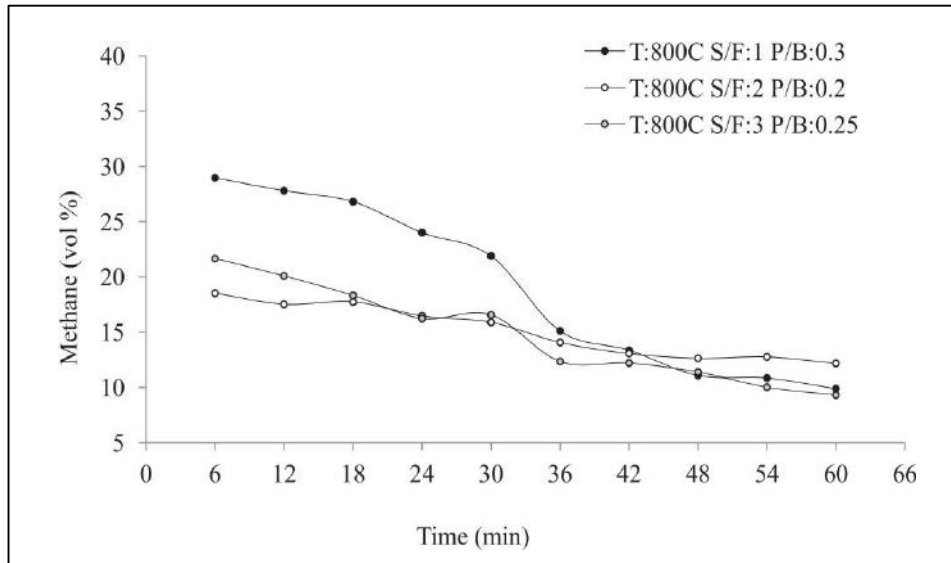


- Total syngas is enriched and achieved maximum value of **87.73 vol%** when mixing polyethylene waste (P) with PKS at temperature of 800°C, S/B of 1, and P/B of 0.3.
- Increased of P in the mixtures increased conversion of the solid feedstock to gaseous products.
- P degrades faster than PKS.

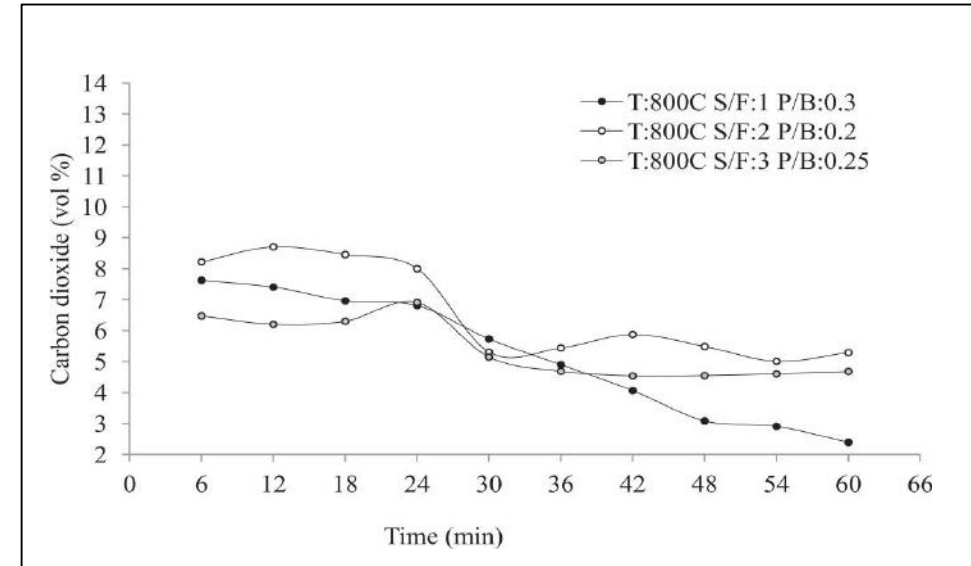
Effect of polyethylene/biomass ratio on syngas production

T: Temperature (°C), S/F: Steam to Biomass Ratio (w/w), P/B: Polyethylene to Biomass Ratio (w/w)





Effect of polyethylene/biomass ratio on methane production



Effect of polyethylene/biomass ratio on carbon dioxide production

T: Temperature ($^{\circ}\text{C}$), S/F: Steam to Biomass Ratio (w/w), P/B: Polyethylene to Biomass Ratio (w/w)

- CH_4 content **increased** from **18.52 vol%** to **28.96 vol%** when **P/B increased from 0.2 w/w to 0.3 w/w**.
- **Reduction of CO_2** content to below than 3 vol% due to Boudouard reaction. Boudouard reaction (endothermic reaction) favored by high temperature of the gasifier leading to the decreased of CO_2 concentration in the gas.



Optimum Condition

The predicted results by Taguchi method were in agreement with the experimental results with maximum standard deviation value of 0.85. CCE is also in agreement with each other with respect to both experimental and predicted value.

	Temp. (°C)	S/F (w/w)	PE/B (w/w)	Catalyst (w/w)	H ₂ (wt%)	CO (wt%)	CO ₂ (wt%)	CH ₄ (wt%)	CCE (wt%)
Actual	800	1	0.30	1.25	76.20	11.60	2.40	10.90	90.20
Prediction	800	1	0.30	1.25	74.50	12.70	3.90	8.90	91.00
Std Dev.	-	-	-	-	0.85	0.11	0.18	0.21	.19

** CCE= Carbon Conversion Efficiency



Kinetic and Thermodynamic Analyses

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Thermo-catalytic co-pyrolysis of palm kernel shell and plastic waste mixtures using bifunctional HZSM-5/limestone catalyst: Kinetic and thermodynamic insights

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ABSTRACT

Kinetic and thermodynamic parameters of catalytic co-pyrolysis of palm kernel shell (PKS) and high-density polyethylene (HDPE) with three different catalysts (zeolite HZSM-5, limestone (LS) and bifunctional HZSM-5/LS) using thermogravimetric analyser via nitrogen environment were studied. The experiments were carried out at different heating rates ranging from 10 to 100 K/min within temperature range of 50–900 °C. Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and modified Distributed Activation Energy Model (DAEM) methods were employed in this current study. The average E_a for PKS, HDPE, PKS/HDPE (2:8) – HZSM-5, PKS/HDPE (2:8) – LS, PKS/HDPE (2:8) – HZSM-5/LS, PKS/HDPE (5:5) – HZSM-5/LS, PKS/HDPE (8:2) – HZSM-5/LS are 137.26–145.49, 247.73–250.45, 168.97–172.50, 149.74–152.79, 115.30–120.39, 124.36–129.41, 151.03–154.47 and 152.67–157.31 kJ mol⁻¹, respectively. Among the different catalysts used, LS demonstrated the lowest average E_a (151.30–120.39 kJ mol⁻¹) and ΔH (109.65–114.74 kJ mol⁻¹). Positive values for ΔH and ΔG were found for the catalytic co-pyrolysis of PKS/HDPE mixtures which indicates the process is in endothermic reaction and possess non-spontaneous nature. The kinetic and thermodynamic analyses revealed the potential of PKS and HDPE as a potential feedstock for clean bioenergy production.

Collaborators:

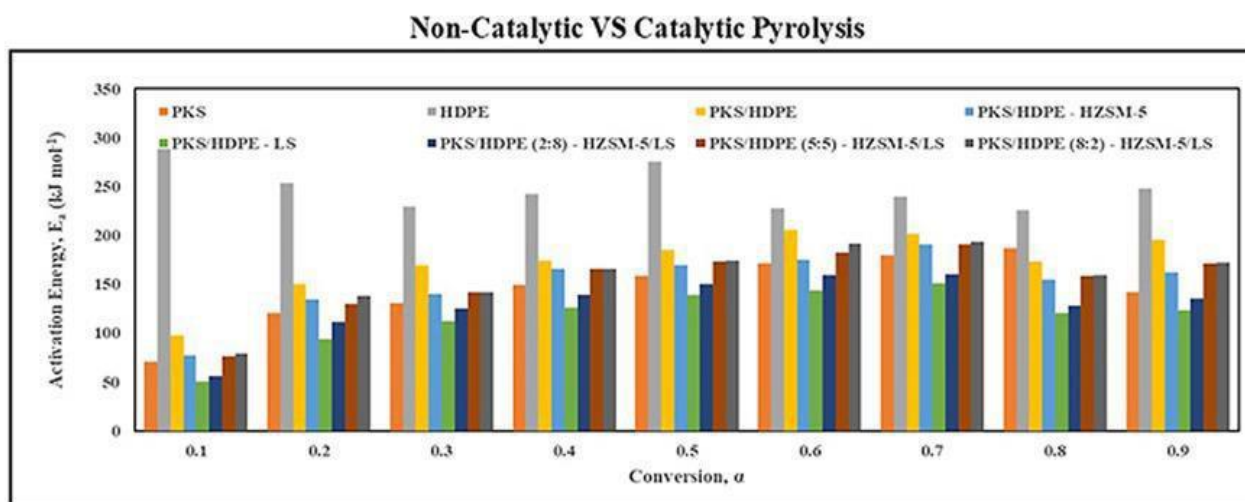
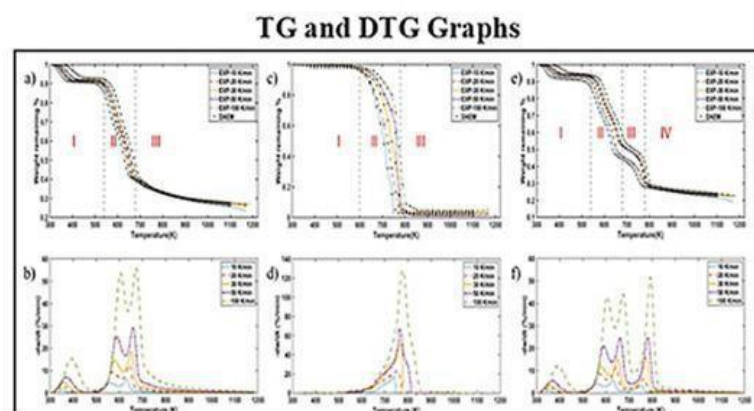
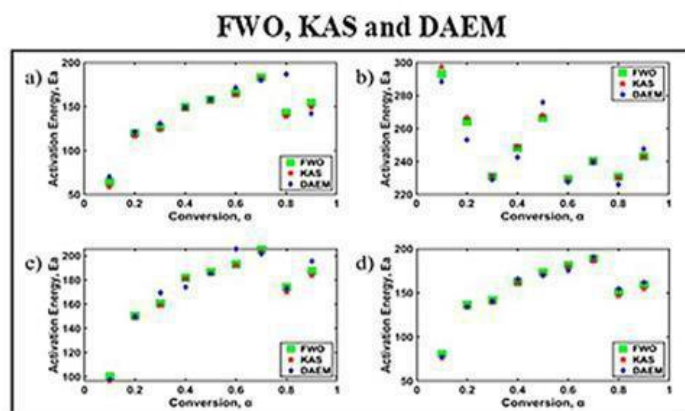
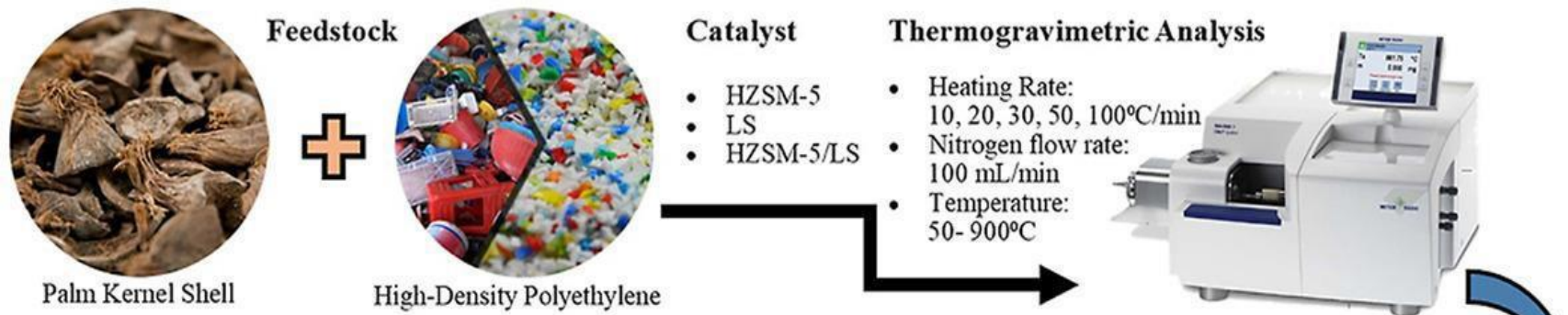


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Key findings:

Feedstock	Average activation Energy, E_a (kJ.mol)
PKS	137.26–145.49
P	247.73–250.45
PKS/P (2:8)	168.97–172.50
PKS/P (8:2)	149.74–152.79
PKS/P (2:8) – HSZM-5/LS	115.30–120.39
PKS/P (8:2) – HSZM-5/LS	152.67–157.31

- Positive values for ΔH and ΔG were found for the catalytic co-pyrolysis of PKS/P mixtures which indicates the process is in endothermic reaction and possess non-spontaneous nature.
- The kinetic and thermodynamic analyses revealed the potential of PKS and P as a potential feedstock for clean bioenergy production.



Challenges Faced and Future Prospects

Challenges Faced

- Removal of CO₂ from product gases through cheap process.
- Production of tar and its conversion into lighter gases.
- Suitable cheap catalyst required for higher syngas yield and gasification efficiency.
- Higher cost of fuel from gasification process as compared to fossil fuels.
- No investment from private sector.

Future Prospects

- Use of adsorbent such as CaO to capture CO₂ at higher temperature.
- Tar production can be reduced using catalyst such as Ni.
- One most important future prospective use of OLGA technique developed by ECN for tar reduction.
- Research should be made for development of new catalyst using conventional (Ni, Fe) and non-conventional catalysts (Coal bottom ash, limestone, etc.).
- Co-generation of power and fuels to reduce the cost and solve the power issue.
- Subsidy in biofuel required.



Concluding Remarks

- Max. syngas yield of 422.40 g syngas/kg feedstock and H₂ yield of 135.27 H₂/kg feedstock were achieved under the optimized condition.
- Optimised condition: *Temperature of 800 °C, P/B of 0.3 w/w, and S/F ratio of 1 w/w based on syngas and H₂ yield.*
- Enhancement of syngas and H₂ production are influenced by the blending of the polyethylene and biomass waste mixtures.
- The kinetic and thermodynamic analyses revealed the potential of PKS and P as a potential feedstock for clean bioenergy production.



Thank you

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