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Gasification of Plastic Waste: Kinetic Evaluation and High Fidelity Numerical Simulation

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Introduction

1. *Waste to energy* is an emerging concept that raps on the abundant and steadily increasing municipal solid waste (MSW) due to urbanization and human development.

2. MSW generation is strongly correlated with human development averaging daily over 1kg in the underdeveloped economy to over 2kg in developed nations. Over 1.7 billion tons of waste has been generate globally in 2015 according to the world-bank at various distribution, but averaging 12% plastics. The heating value of the plastic is greater than the average grades of coal and petroleum coke present in the US [1].

3. Plastics being flexible, durable and expensive lending its increasing usage and disposal [2, 3].

4. Polyethylene takes the lion share of 50-60% fraction followed with polypropylene at 25-35% and the remaining split between polystyrene, terephthalate and PVC. As plastic segregation is becoming a popular practice rendering its availability as a single waste stream that facilitates recycling or conversion.

5. Gasification is considered a mature and proven technology for a variety of feedstock including coal, biomass, auto-shredder residue, and fossil fuels. However, gasification of MSW or its segregated derivatives such as plastics is relatively recent, and is facing number of technical barriers [4].

[1] "Energy and economic value of non-recycled plastics (NRP) and municipal solid wastes (MSW) that are currently landfilled in the fifty states"- Earth Engineering Center, Columbia University, August 2011.
[2] Hester, Ronald E.; Harrison, R. M. (editors) (2011). Marine Pollution and Human Health. Royal Society of Chemistry. pp. 84-85. ISBN 184973240X.
[3] Hammer, J; Kraak, MH; Parsons, JR (2012). "Plastics in the marine environment: the dark side of a modern gift". Reviews of environmental contamination and toxicology. 220: 1–44. doi:10.1007/978-1-4614-3414-6_1
[4] Gershman, Brickner and Bratton, solid waste management consultants: Gasification of Non-Recycled PlasticsFrom Municipal Solid Waste In the United States, The American Chemistry Council, GBB/12038-01 August 13, 2013, www.gbbinc.com

Introduction

There is limited literature on plastic gasification compared to coal and their co-gasification.

1. *Alvarez and coworker* investigated the co-gasification of plastic (20%) biomass (80%) mixtures and reported the addition of plastic increase H_2 syngas fraction and also indicated that PP is more favorable for H_2 production than PS [1].
2. *Straka and Bicakova* reported insignificant effect on composition properties or amount of gas obtained in their attempt to obtain a richer H_2 gas when 20% waste plastic is co-gasified with low sulfur and ash contents lignite [2].
3. Arena and Gregorio also demonstrated the feasibility of the air plastic gasification in 400kw pilot scale fluidized bed reactor [3]. They investigate the role of the equivalence ratio (ER) and reported large tar particulate formation, as well as acid/basic gases aside to the syngas. They also stated the sensitivity of the reactor to the different waste plastics.
4. *Kim et al* conducted air gasification of plastic and they study the influence of ER, reactor temperature, and feed size as well as additives such as active carbon and dolomite in the reducing the tar and increasing the productivity of H_2 [4]. Their optimal equivalence ratio to produce clear syngas was near 0.21 at an average LHV of 13.44MJ/m^3. Their findings suggested the favorability of active carbon over dolomite for tar reduction in the syngas stream.
5. *Xiao et al* carried out experimental study on air gasification of PP in a fluidized bed gasifier (0.1m dia by 4.2 m height) [5]. They investigated the role of ER, reactor height, fluidization velocity on the product yield, gas composition, heating value. ER showed to have the greatest effect on the temperature and gas composition and is directly proportional to the formation of fuel gas and decrease the formation of tars and char. The bed height and fluidization velocity showed to have much lesser influence. They suggested the feasibility of PP gasification leading to the production of low tar contents syngas ranging from 5.2-11.4 MJ/N.m^3 [5].
6. *Wu and Williams* carried out catalytic gasification of the post-consumer plastic waste from MSW and have studied the catalyst amount, temperature, and water injection. They observed the pronounced influence of the temperature and water contents on the syngas yield and H_2 production compared to the sweeping in catalytic: plastic ratio. They suggested the effectiveness catalyst loading 0.5g/g that continually reducing the coke/tar formation [6].

[1] Jon Alvarez, Shogo Kumagai, Chunfei Wu, Toshiaki Yoshioka, Javier Bilbao, Martin Olazar, Paul T. Williams, Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification, International Journal of Hydrogen Energy, Volume 39, Issue 21, 15 July 2014, Pages 10883–10891
[2] Pavel Straka, Olga Bičáková, Hydrogen-rich gas as a product of two-stage co-gasification of lignite/waste plastics mixtures, i n t e r n a t i o n a l journal o f hydrogen energy Volume 39, Issue 21, 15 July 2014, Pages 10987–1099
[3] Umberto Arena, Fabrizio Di Gregorio, Energy generation by air gasification of two industrial plastic wastes in a pilot scale fluidized bed reactor, Energy, Volume 68, 15 April 2014, Pages 735–743
[4] Jin-Won Kim, Tae-Young Mun, Jin-O Kim, Joo-Sik Kim, Air gasification of mixed plastic wastes using a two-stage gasifier for the production of producer gas with low tar and a high caloric value, Fuel, 90 (2011) 2266–2272.
[5] Rui Xiao, Baosheng Jin, Hongcang Zhou, Zhaoping Zhong, Mingyao Zhang, Air gasification of polypropylene plastic waste in fluidized bed gasifier, Energy Conversion and Management 48 (2007) 778–786
[6] Chunfei Wu, Paul T. Williams, Pyrolysis–gasification of post-consumer municipal solid plastic waste for hydrogen production, International Journal of hydrogen energy 35 (2010) 949–957.

Introduction

High fidelity modelling is mature tool to study a reactive complex flow. It requires accurate analysis of the kinetic data for both devolatalization/pyrolysis.

1. *Lee et al* have used CFD to numerically model the circulating fluidized bed gasifier for the plastic waste in an Eulerian-Granular approach [1]. Their attempt were more focus on the circulating of the particle while no gasification/reaction were considered. They however study the change of the fluidized velocity and the particle size circulation.

2. *Gao et al* studied thermal degradation at inert gas conditions for HDPE sample using the two methods. Dynamic heating was conducted a set of five heating rates, 4, 6, 8, 10 and 20 ^{o}C /min, whereas the isothermal was carried at three different temperatures, 440, 450, and 460 ^{o}C. The reported activation energy for dynamic and isothermal are respectively 194.8 KJ/mole and 201.5 KJ/mole [2] .

3. *Bockhorn et al* investigated the thermal degradation of PE and PP under helium environment, 0.1Mpa pressure, and at temperature range between 410 and 480 ^{o}C and reported activation energy of 262.1 KJ/mole and 268$\pm$3 KJ/mole as well as 223.7$\pm$1.6 KJ/mole and 220$\pm$5 KJ/mole for PE and PP under dynamic and isothermal conditions, respectively [3].

4. Costa et al reported activation energies for PE ranges from 160-320 kJ/mole and pre-exponential ranging from 10E11 to 10E21 sec^{-1} [4].

[1] Ji Eun Lee, Hang Seok Choi, Yong Chil Seo, Study of hydrodynamic characteristics in a circulating fluidized bed gasifier for plastic waste by computational fluid dynamics modeling and simulation, Journal of Material Cycles and Waste Management, October 2014, Volume 16, Issue 4, pp 665–676
[2] Gao, Z., I. Amasaki, and M. Nakada, A thermogravimetric study on thermal degradation of polyethylene. Journal of Analytical and Applied Pyrolysis,. 67,1, (2003), 1-9.
[3] Bockhorn, H., et al., Kinetic study on the thermal degradation of polypropylene and polyethylene. Journal of Analytical and Applied Pyrolysis, 1999. 48(2): p. 93-109.
[4] Costa, P.A., et al., Kinetic evaluation of the pyrolysis of polyethylene waste. Energy & Fuels, 2007. 21(5): p. 2489-2498.

Objectives

- It should be emphasize that despite the progress made to date on both experimental and modeling studies of plastic gasification, a wide range of research and development program is lacking on this subject. Current implementations are limited to pilot scale pyrolysis which continue to be challenging and very sensitive process.

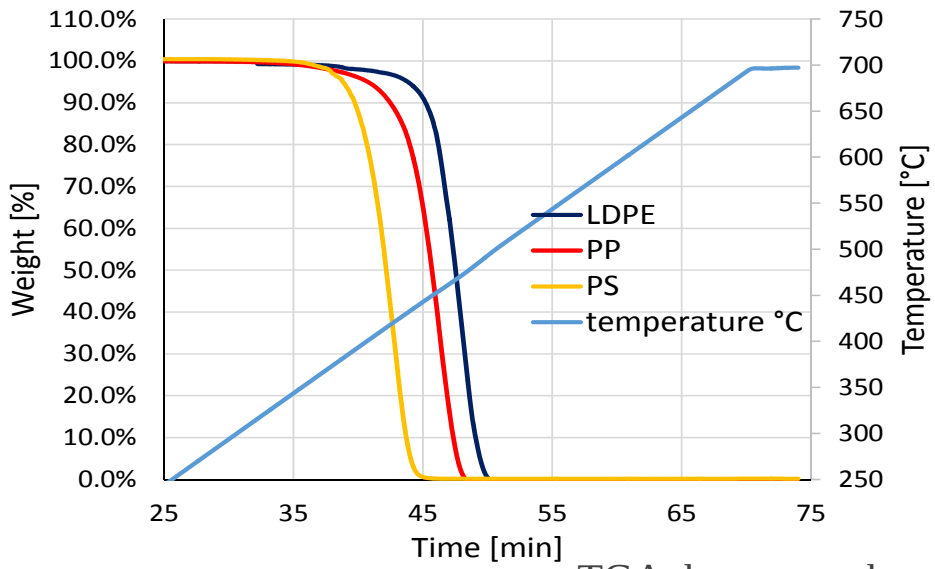
- Gasification of plastic blends is an emerging technology as this source will continue to grow that requires strong need for detailed gasification investigations covering the different plastic types and their mixtures.

- This work addresses this need by:

  - ✓ Assessing the proximate and ultimate analyses
  - ✓ Conduct TGA/DSC analysis to infer the kinetics of the plastic reaction.
  - ✓ Carry out high fidelity inside an entrained flow gasifier simulated in a drop tube reactor environment.

Materials and Method: Material characterization

1. Thermo-Gravimetric and elemental analyses are conducted on the three common types of plastics, PE, PP and PS samples: Source Borogue/Borealis Company UAE.
2. These plastic samples are sold under Borogue commercial trading in sealed plastic bags of 5kg in the form of small granules of 20-50 µg size.
3. Single granule of multiple samples are subjected to TGA proximate and ultimate/elemental analyses using STDQ600 and FLASH 200 respectively



TGA thermograph measurements of LDPE, PP and PS

Materials and Method: Material characterization

Proximate and Ultimate Analyses of LDP, PP and PS

Prox. & Ultimate Analysis (Wt. %)	LDPE	PP	PS
Moisture	0.11	0.12	0.09
Volatile	99.816	99.821	99.814
Fixed Carbon	0.051	0.042	0.071
Ash	0.023	0.017	0.025
HV (MJ/kg)	43.363	40.965	40.985
Carbon	24.00	36.00	96.00
Hydrogen	4.00	6.00	8.00
Nitrogen/Oxygen/Sulfur	0.00	0.00	0.00

The mass fraction of organic elements the heat of formation can be estimated by [1]:

$$HHV\,[MJ\ /\ kg] = 0.3491\ Y_C + 1.1783\ Y_H - 0.1043\ Y_O$$

Chemical formula for LDPE, PP and PS

Mixture	Chemical Formula	Measured HV(MJ/kg)	Estimated HV (MJ/kg)	Abs Error in HV (%)
LDPE	$(C_2H_4)n$	43.363±0.15	46.7557143	7.824
PP	$(C_3H_6)n$	40.965±0.18	46.7557143	14.136
PS	$(C_8H_8)n$	40.985±0.21	41.2884615	0.740

[1] Green, A. and S. Sadrameli, Analytical representations of experimental polyethylene pyrolysis yields. Journal of Analytical and Applied Pyrolysis, 2004. 72(2): p. 329-335.

$$HHV\ [MJ\ /\ kg] = 0.3491\ Y_C + 1.1783\ Y_H - 0.1043\ Y_O$$

Materials and Method: Modeling setup

The gasification of the plastics includes several process events including moisture release, devolatalization, gas phase reactions and to lower extent potential char combustion. These can be illustrated as:

$$Feedstock_s \rightarrow Steam + Volatile_s + Char_s\ (C_s Ash)$$

$$Volatile_s \rightarrow \alpha_1 CH_4 + \alpha_2 CO + \alpha_3 CO_2 + \alpha_4 H_2 + \alpha_5 H_2O + \alpha_6 Tar$$

$$C_s Ash + 0.5 O_2 \rightarrow CO + Ash$$

$$C_s Ash + CO_2 \rightarrow 2CO + Ash$$

$$C_s Ash + H_2O \rightarrow CO + H_2 + Ash$$

Materials and Method: Kinetic study

As moisture is nearly absent from plastic, devolatalization reaction may proceed under the constrain of conservation of mass and energy:

$$C_n H_m + heat \rightarrow devolatalization\ components$$

Using the TGA/DTG experimental data, the overall devolatalization reaction can be modeled as:

$$\frac{dX}{dt} = Ae^{-E/RT}(1-X)^n \quad or \quad \frac{dX}{(1-X)^n} = \beta Ae^{-E/RT}dT$$

Where X the mass loss fraction ($X = (w_o - w)/(w_o - w_f)$

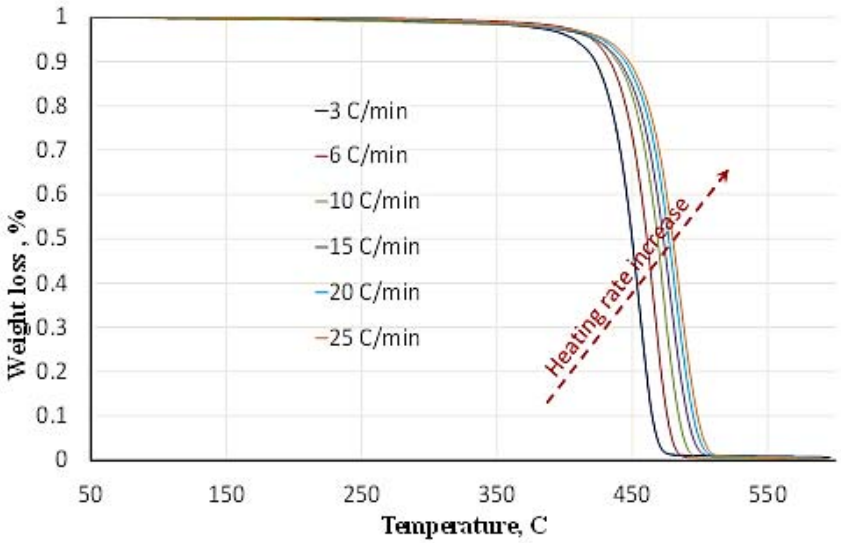
Arrhenius method is simple to use and can lead to direct extraction of E from the slope of the linear fit of log [dw/dt/w] versus 1/T based on the following form of eq:

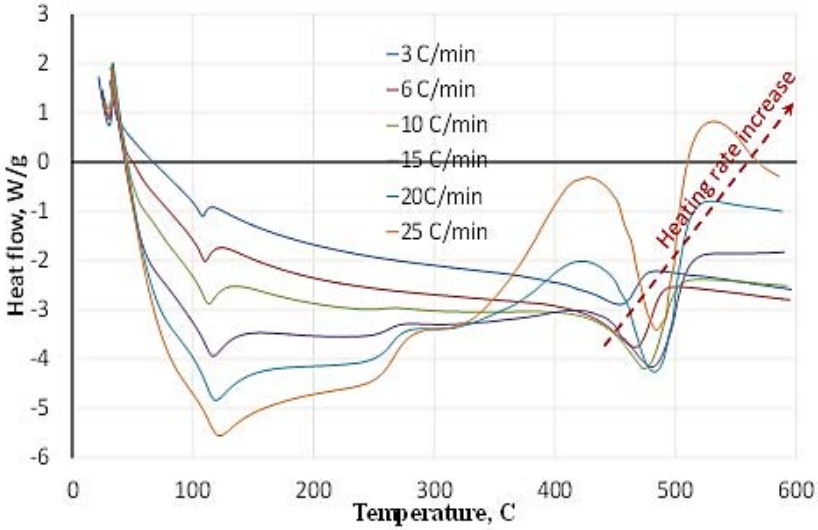
$$\log[dw/dt/w] = \log A - E/2.303RT$$

Coats and Redferm the activation energy is determined from the slope of ln [g(x)/T^2]versus 1/T plot as:

$$ln\left(\frac{g(x)}{T^2}\right) = ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}$$

Materials and Method: Kinetic study

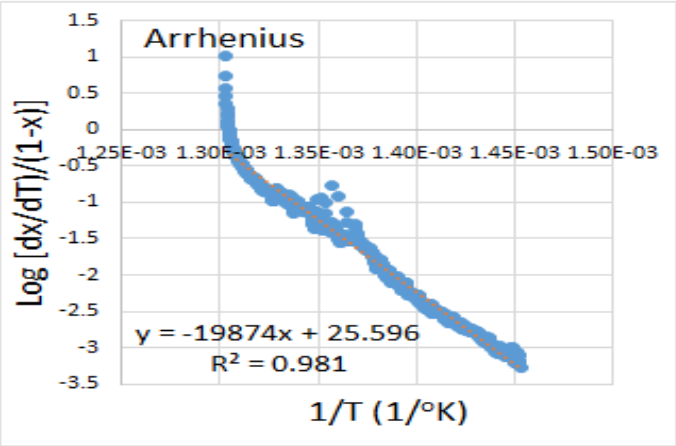


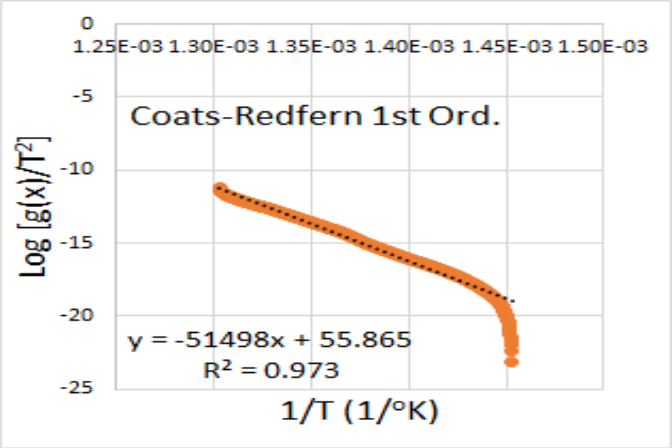


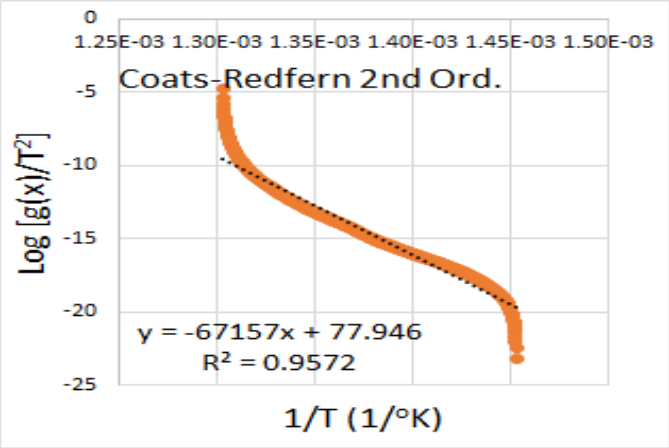
TGA and DSC corresponds to different heating rates of the LDPE

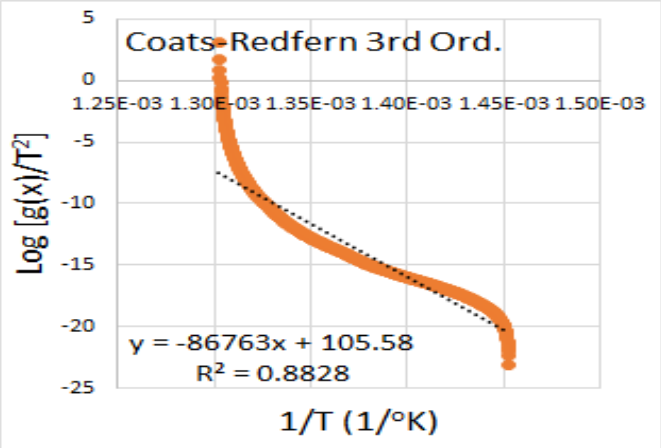
Materials and Method: Kinetic study

Representation of Arrhenius model and 1st , 2nd and the 3rd order Coats-Redfern model data:









Materials and Method: Kinetic study

The evaluated kinetic data for the LDPE, PP and PS based on Arrhenius, and Coats-Redfern, 1st , 2nd and the 3rd order models.

LDPE	Slope	Intercept	R^2	E (KJ/mol)	A (1/sec)
Arrhenius	-19874	25.596	0.9810	380.5303	6.570E+23
Coats-Redfern 1st	**-51498**	**55.865**	**0.9730**	**428.1544**	**1.569E+28**
Coats-Redfern 2nd	-67157	77.746	0.9572	558.3433	6.510E+37
Coats-Redfern 34d	-86763	105.58	0.8828	721.3476	1.030E+50
PP	Slope	Intercept	R^2	E (KJ/mol)	A (1/sec)
Arrhenius	-11498	14.578	0.9308	220.1538	6.310E+12
Coats-Redfern 1st	**-26350**	**23.016**	**0.9672**	**219.0739**	**4.349E+13**
Coats-Redfern 2nd	-32004	31.625	0.9001	266.0813	2.895E+17
Coats-Redfern 3rd	-39007	42.280	0.7947	324.3042	1.496E+22
PS	Slope	Intercept	R^2	E (KJ/mol)	A (1/sec)
Arrhenius	-13630	18.540	0.9424	260.9755	5.780E+16
Coats-Redfern 1st	**-39108**	**43.389**	**0.9501**	**325.1439**	**4.547E+22**
Coats-Redfern 2nd	-69470	89.215	0.9586	577.5736	6.445E+42
Coats-Redfern 3rd	-107330	146.35	0.8986	892.3416	6.480E+67

Materials and Method: Kinetic study

- Kinetic data for the devolatalization reactions:

Component	Reaction	Activation Energy (E_a kJ/mol)	Pre-Exponential Factor (A 1/s)
PE	$3(C_2H_4)_n \rightarrow 2nC_{2.141}H_{2.126} + 1.156nH_2 + nC_{1.718}H_{5.436}$	380.5303	1.569×10^{28}
PP	$(C_3H_6)_n \rightarrow nC_{2.141}H_{2.126} + 0.078nH_2 + nC_{0.859}H_{3.718}$	219.0739	4.349×10^{13}
PS	$(C_8H_8)_n \rightarrow 3nC_{2.306}H_{1.145} + 0.2005nH_2 + nC_{1.082}H_{4.164}$	325.1439	4.547×10^{22}

- Kinetic Data for the Homogeneous Reactions [1]:

Reaction	Activation Energy, E_a ($\frac{J}{mol}$)	Pre-Exponential Factor, A (sec^{-1})	N
$C_nH_m + \left(\frac{n}{2}\right)O_2 \rightarrow nCO + \frac{m}{2}H_2$	1.25×10^8	4.4×10^{11}	0
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	1.67×10^8	6.8×10^{15}	-1
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	1.67×10^8	2.24×10^{12}	0
$CO + H_2O \rightarrow CO_2 + H_2$	8.37×10^7	2.75×10^9	0

- Kinetic Data for the Heterogeneous Reactions [1]:

Reaction	Activation Energy, E_a ($\frac{J}{mol}$)	Pre-Exponential Factor, A (sec^{-1})	N
$C + \frac{1}{2}O_2 \rightarrow CO$	9.23×10^7	2.3	1
$C + CO_2 \rightarrow 2CO$	1.62×10^8	4.4	1
$C + H_2O \rightarrow CO + H_2$	1.47×10^8	1.33	1

Watanabe, H. and M. Otaka, Numerical simulation of coal gasification in entrained flow coal gasifier. Fuel, 2006. 85(12-13): p. 1935-1943.

Materials and Method: Modeling equation

Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho v_x)}{\partial t} + \frac{\partial(\rho v_r)}{\partial t} + \frac{\rho v_r}{r} = S_m$$

Conservation of momentum:

$$\frac{\partial(\rho v_x)}{\partial t} + \frac{1}{r}\frac{\partial}{\partial x}(r\rho v_x v_x) + \frac{1}{r}\frac{\partial}{\partial r}(r\rho v_r v_x) = -\frac{\partial p}{\partial x} + \frac{1}{r}\frac{\partial}{\partial x}\left[\mathrm{r}\mu\left(2\frac{\partial v_x}{\partial x} - \frac{2}{3}(\nabla\cdot\vec{v})\right)\right] + \frac{1}{r}\frac{\partial}{\partial r}\left[\mathrm{r}\mu\left(\frac{\partial v_x}{\partial r} + \frac{\partial v_r}{\partial x}\right)\right] + F_x$$

$$\frac{\partial(\rho v_r)}{\partial t} + \frac{1}{r}\frac{\partial}{\partial x}(r\rho v_x v_r) + \frac{1}{r}\frac{\partial}{\partial r}(r\rho v_r v_r) = -\frac{\partial p}{\partial x} + \frac{1}{r}\frac{\partial}{\partial x}[\mathrm{r}\mu(\frac{\partial v_x}{\partial r} + \frac{\partial v_r}{\partial x})] + \frac{1}{r}\frac{\partial}{\partial r}\left[\mathrm{r}\mu\left(2\frac{\partial v_r}{\partial r} - \frac{2}{3}(\nabla\cdot\vec{v})\right)\right] - 2\mu\frac{v_r}{r^2} + \frac{2}{3}\frac{\mu}{r}(\nabla\cdot\vec{v}) + \rho\frac{{v_z}^2}{r} + F_r$$

Conservation of energy:

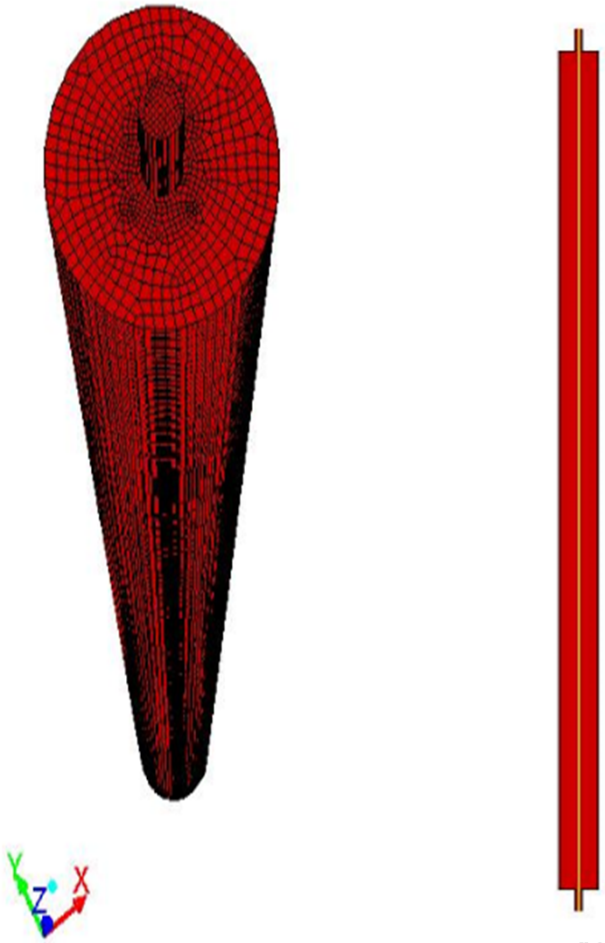
$$\frac{\partial(\rho E)}{\partial t} + \nabla\cdot\left(\vec{v}(\rho E + p)\right) = \nabla\cdot\left(k_{eff}\nabla T - \sum_j h_j\vec{J}_j + (\bar{\bar{\tau}}_{eff}\cdot\vec{v})\right) + S_h$$

Where $E = h - \frac{p}{\rho} + \frac{v^2}{2}$

And $h = \sum_j Y_j h_j$

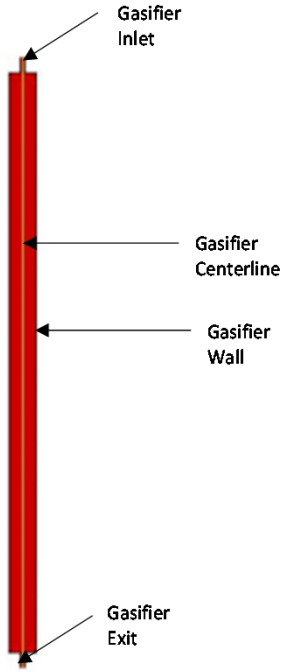
Conservation of species:

$$\frac{\partial(\rho Y_i)}{\partial t} + \nabla\cdot(\rho\vec{v}Y_i) = -\nabla\cdot\vec{J}_i + R_i + S_i$$

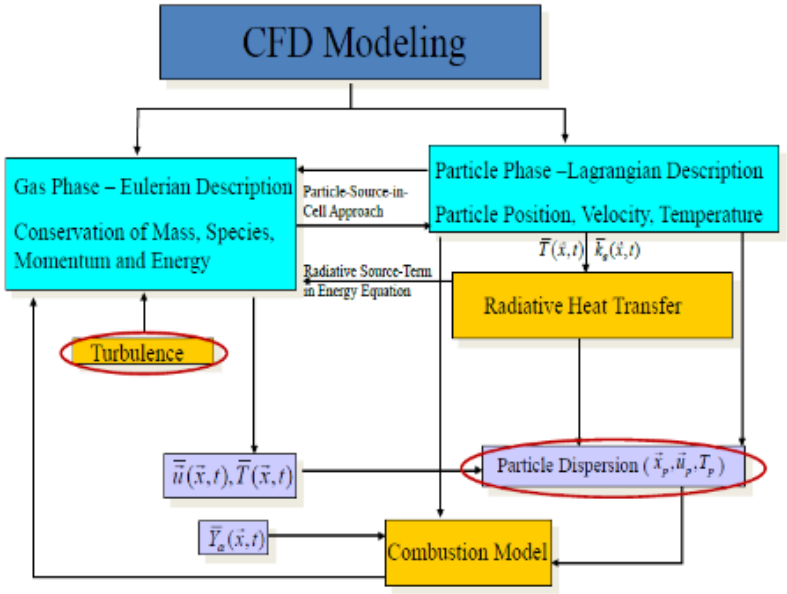


Materials and Method: Boundary conditions and numerical solution

Boundary Condition	Value (Coal)
Length of Gasifier	1540 mm
Outer Diameter of Gasifier	75 mm
Inner Diameter of Gasifier	66 mm
Mass Flow Inlet	1.3320 g/s
Outer Wall Temperature	1,100C



Geometry configuration and gasifier boundary conditions

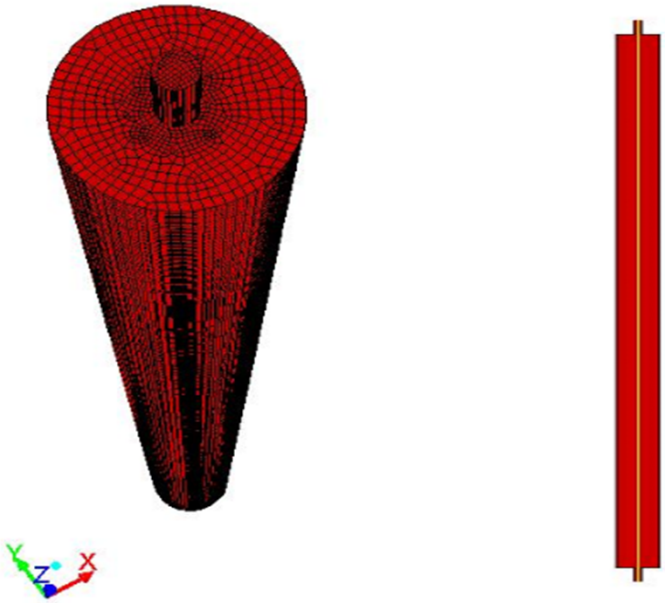


Numerical solution approach for gasification [1]

[1] Adeyemi, I., Janajreh, I., Arink, T., & Ghenai, C. (2017). Gasification behavior of coal and woody biomass: Validation and parametrical study. Applied Energy, 185, 1007-1018.

Results: Kinetic study results

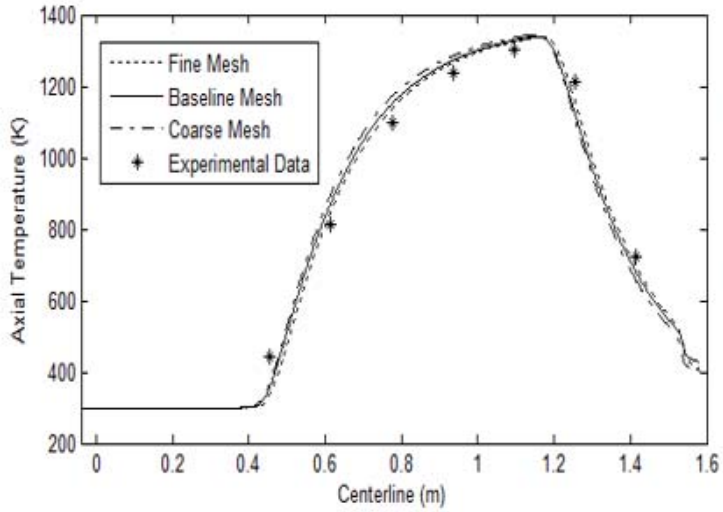
Mesh Sensitivity Studies, Scale Effect and Model Validation

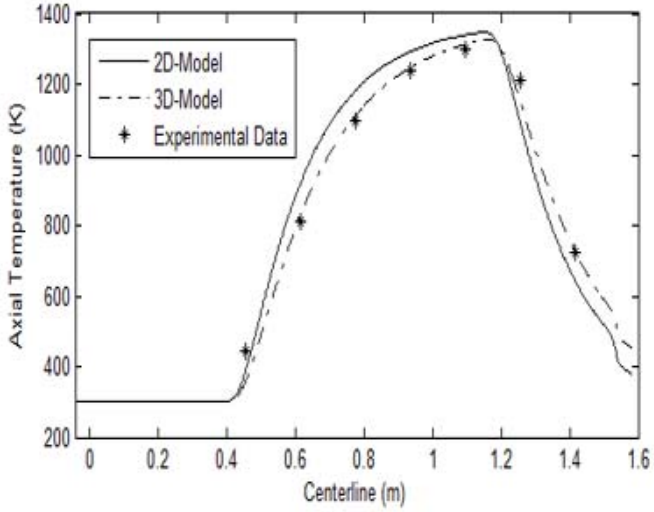


The 2D and 3D mesh structure

Details of the 2D meshes used for sensitivity analysis

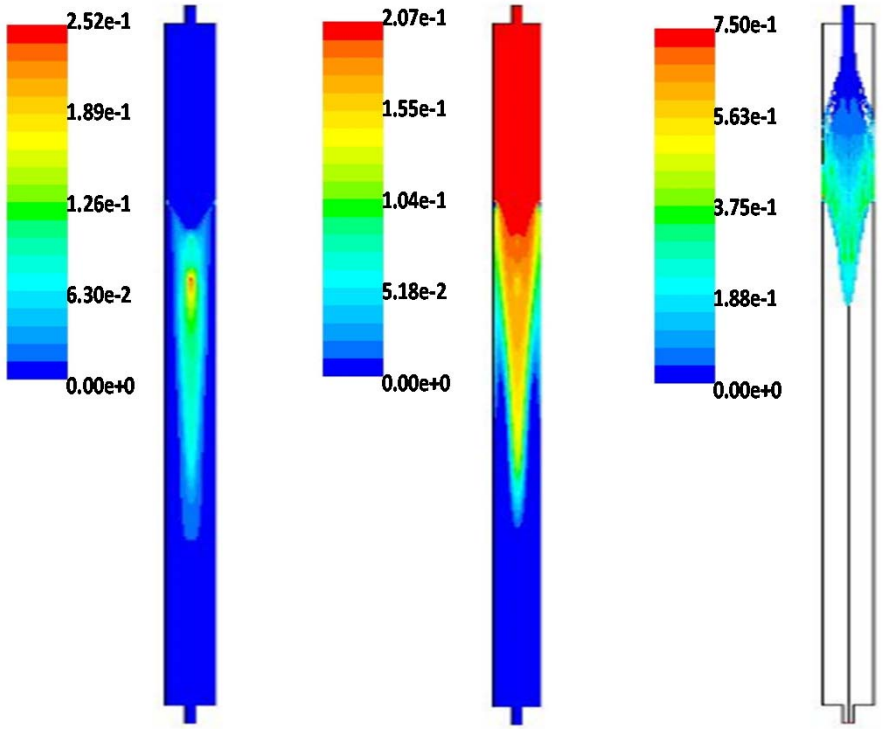
Mesh Type	Number of Cells	Number of Faces	Number of Nodes
Coarse	13,210	25,593	14,038
Baseline	68,680	135,686	70,355
Fine	142,525	282,294	145,282



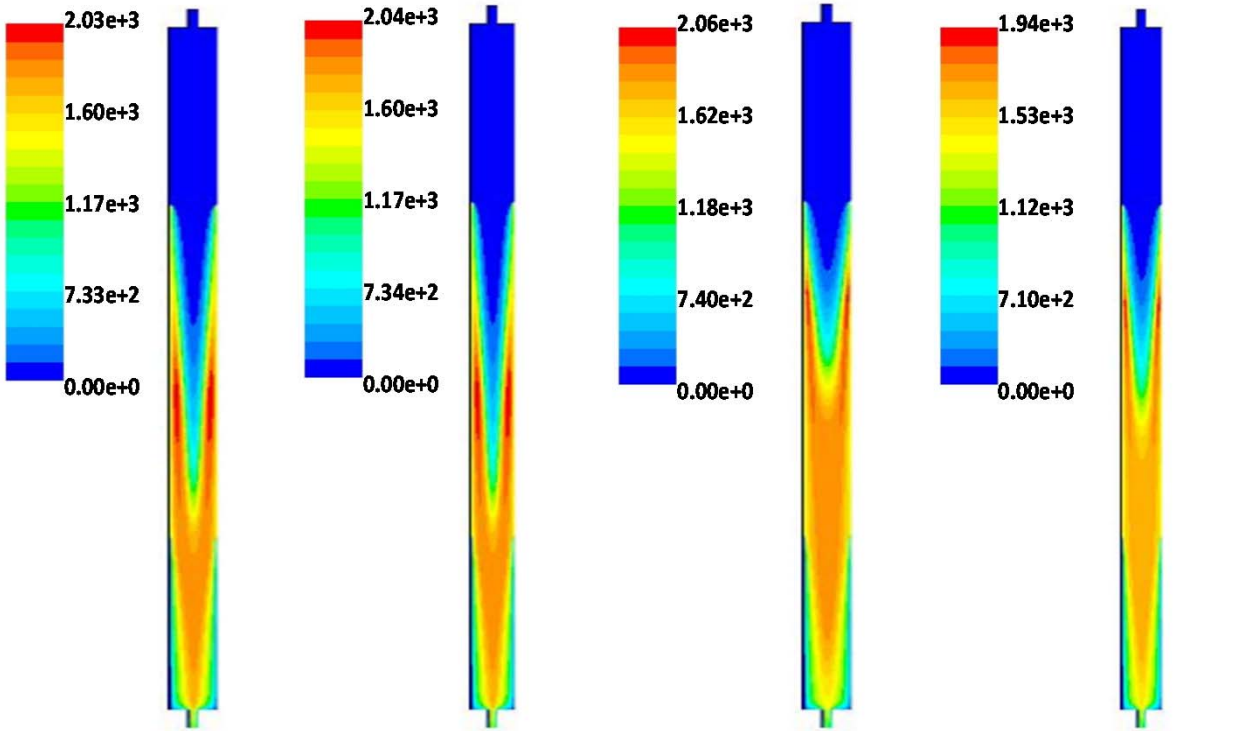


Results: Gasification phenomena

The Vol & O2 mole fractions contour and particle tracking



(a) Volatile Mole Fraction (b) Oxygen Mole Fraction (c) Particle Tracking

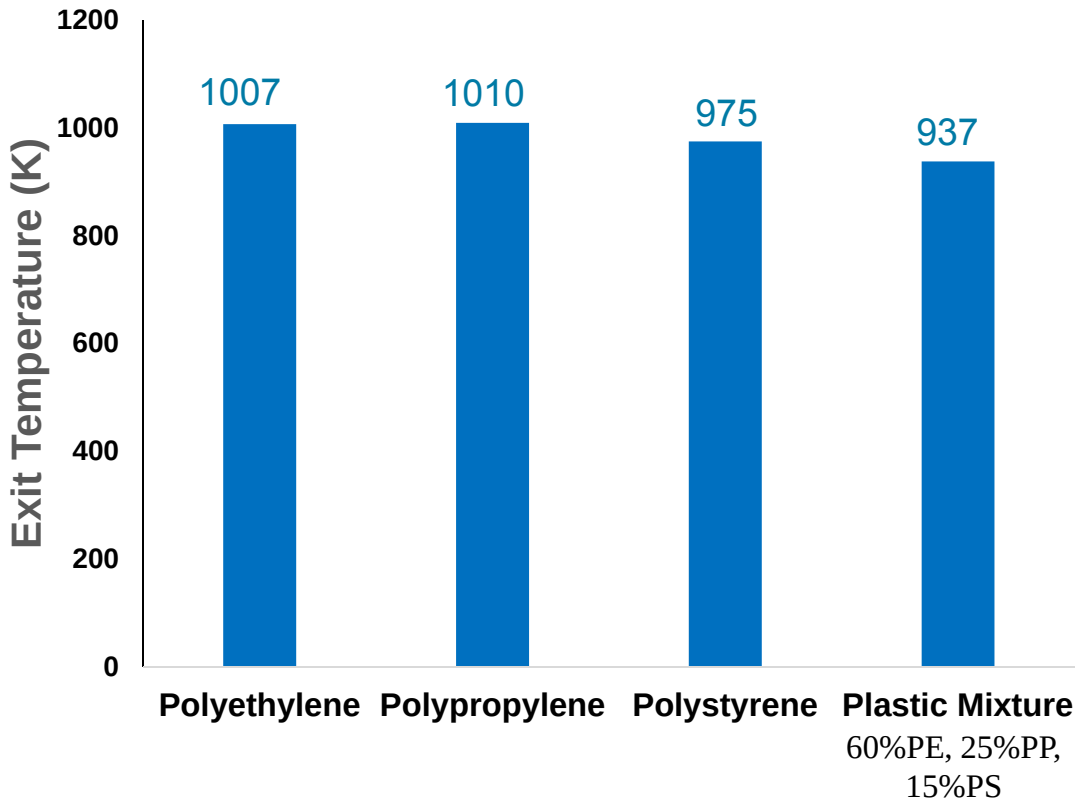


(a) Polyethylene (b) Polypropylene (c) Polystyrene (d) Plastic Mixture

60%PE, 25%PP, 15%PS

The isothermal Temperature contours for the four plastics (in K)

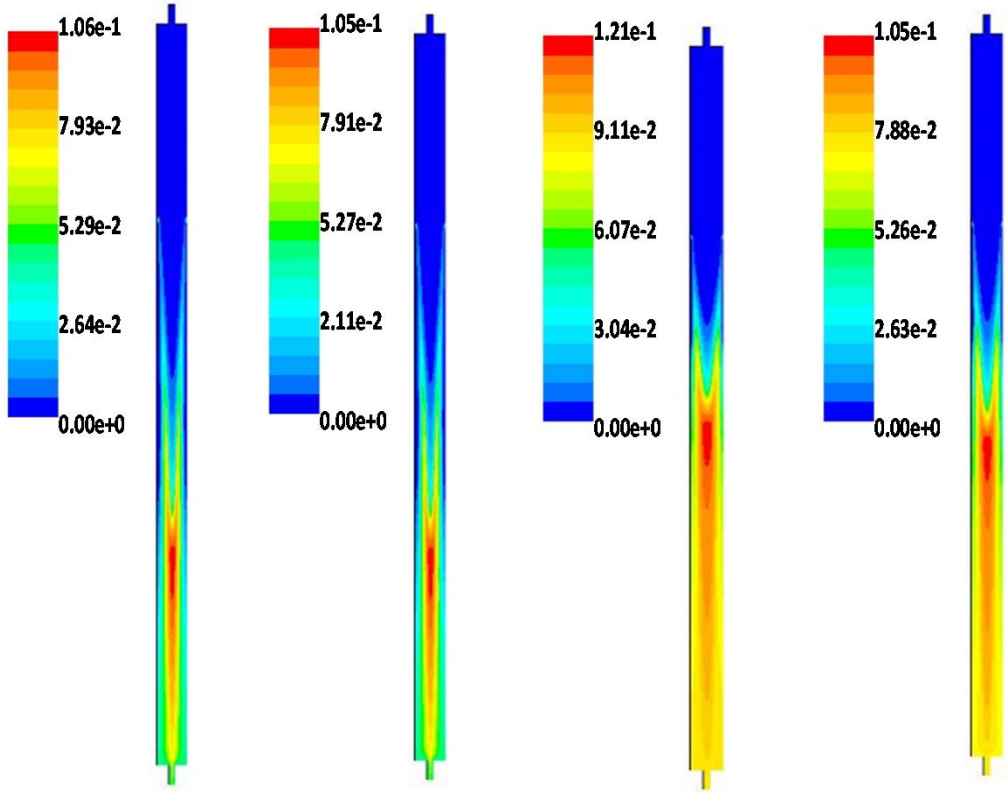
Results: Gasification phenomena



The exit temperature for the four plastic particles

Results: Syngas Production and Gasification Performance

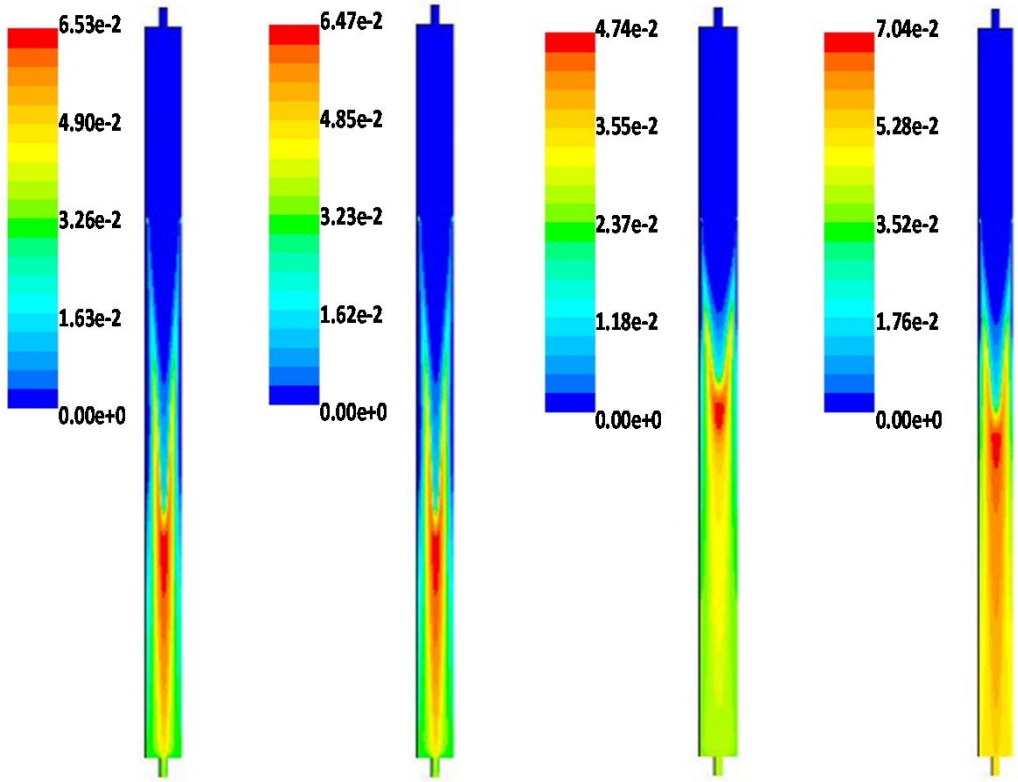
Mole fraction of CO



(a) Polyethylene (b) Polypropylene (c) Polystyrene (d) Plastic Mixture

60%PE, 25%PP, 15%PS

Mole fraction of H_2

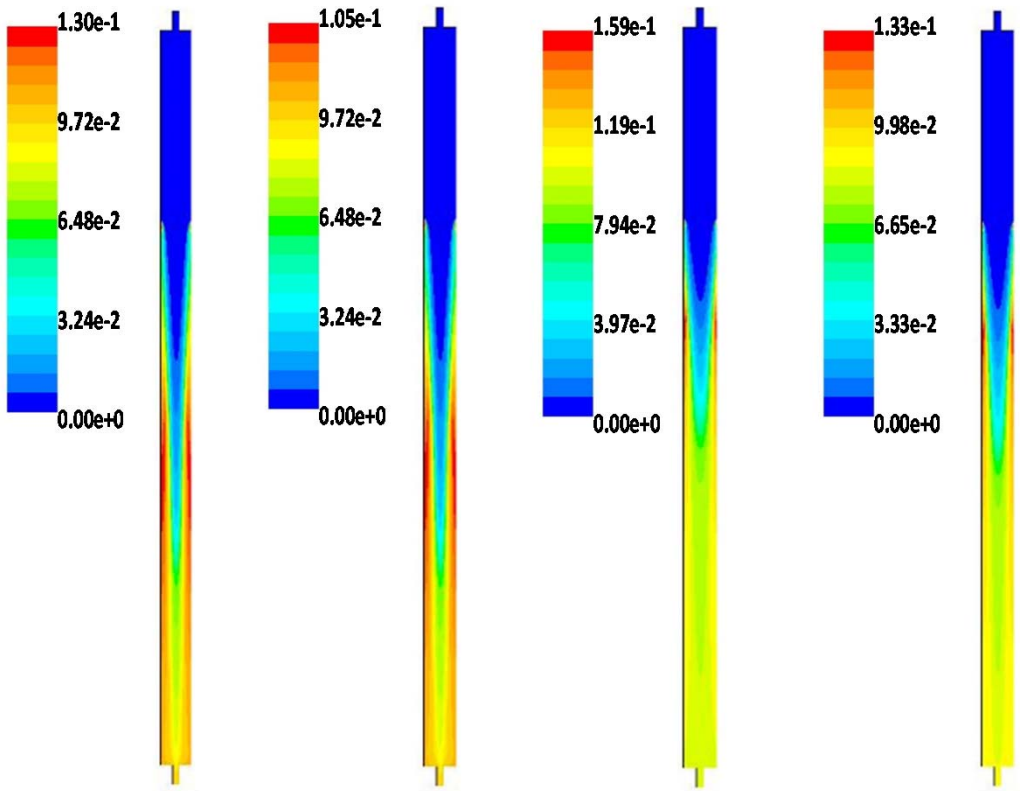


(a) Polyethylene (b) Polypropylene (c) Polystyrene (d) Plastic Mixture

60%PE, 25%PP, 15%PS

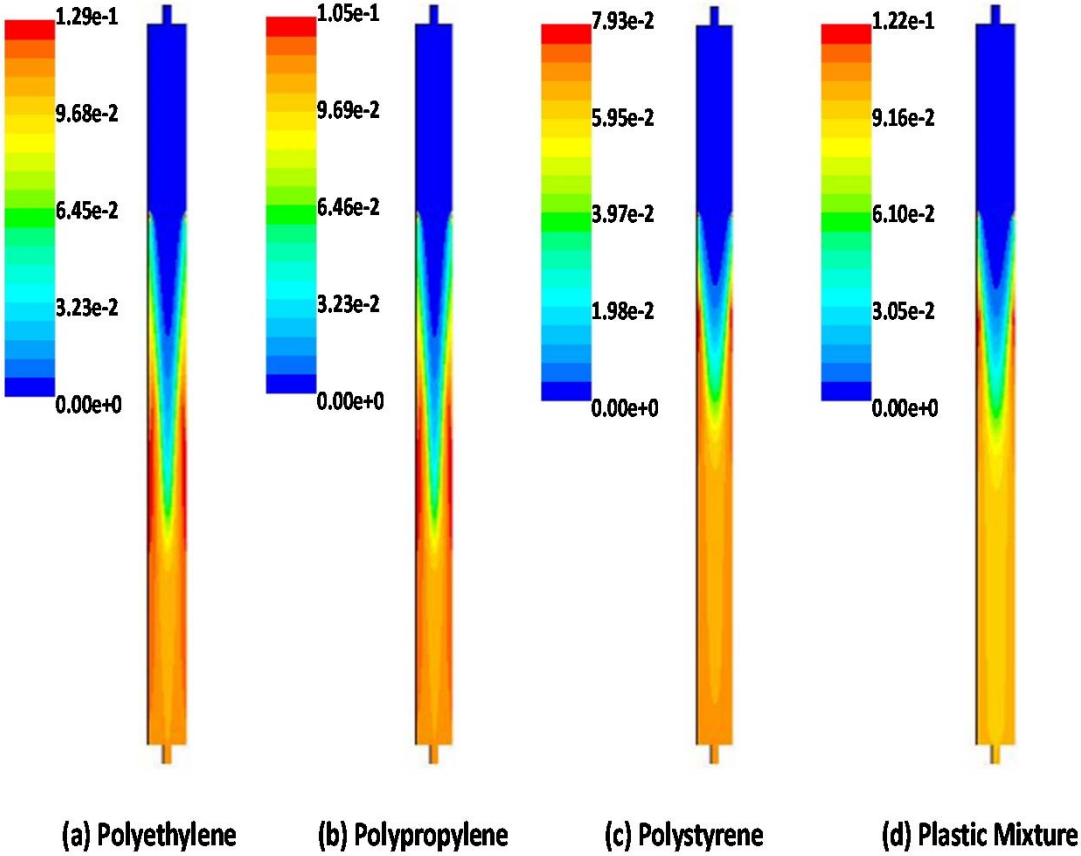
Results: Syngas Production and Gasification Performance

Mole fraction of CO_2



(a) Polyethylene (b) Polypropylene (c) Polystyrene (d) Plastic Mixture

60%PE, 25%PP, 15%PS

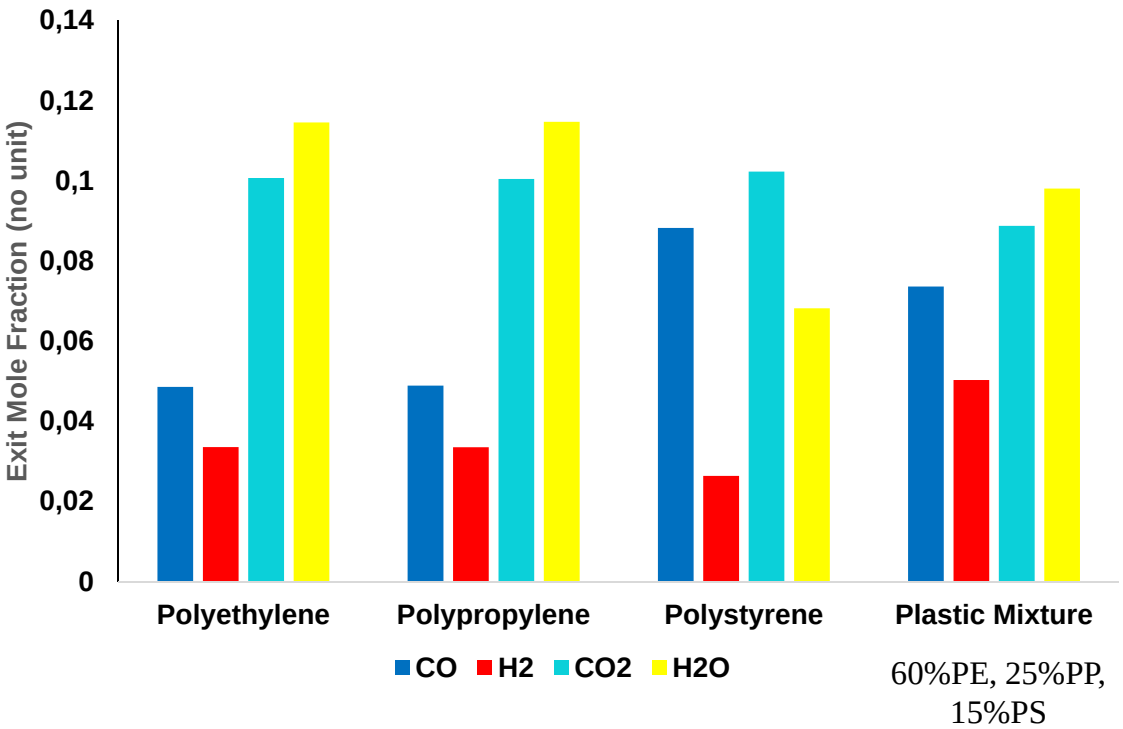


(a) Polyethylene (b) Polypropylene (c) Polystyrene (d) Plastic Mixture

Mole fraction of H_2O

60%PE, 25%PP, 15%PS

Results: Syngas Production and Gasification Performance

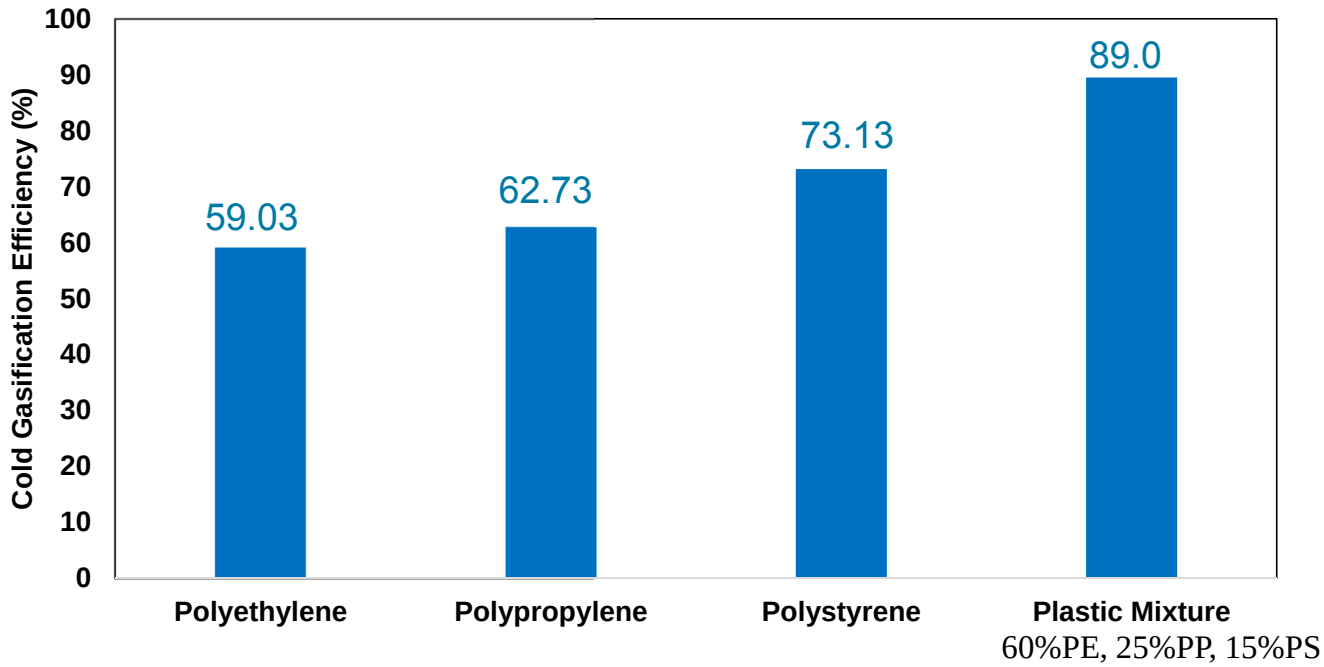


The exit mole fraction for the four plastic particles

Results: Syngas Production and Gasification Performance

The cold gasification efficiency for the four plastic types were estimated based on the expression given by Skodras et al. [1].

$$CGE(\%) = \frac{\dot{m}_{out}\,(y_{H_2} HHV_{H_2} + y_{CO} HHV_{CO} + y_{CH_4} HHV_{CH_4})}{\dot{m}_{in,fuel}\, HHV_{fuel}}$$

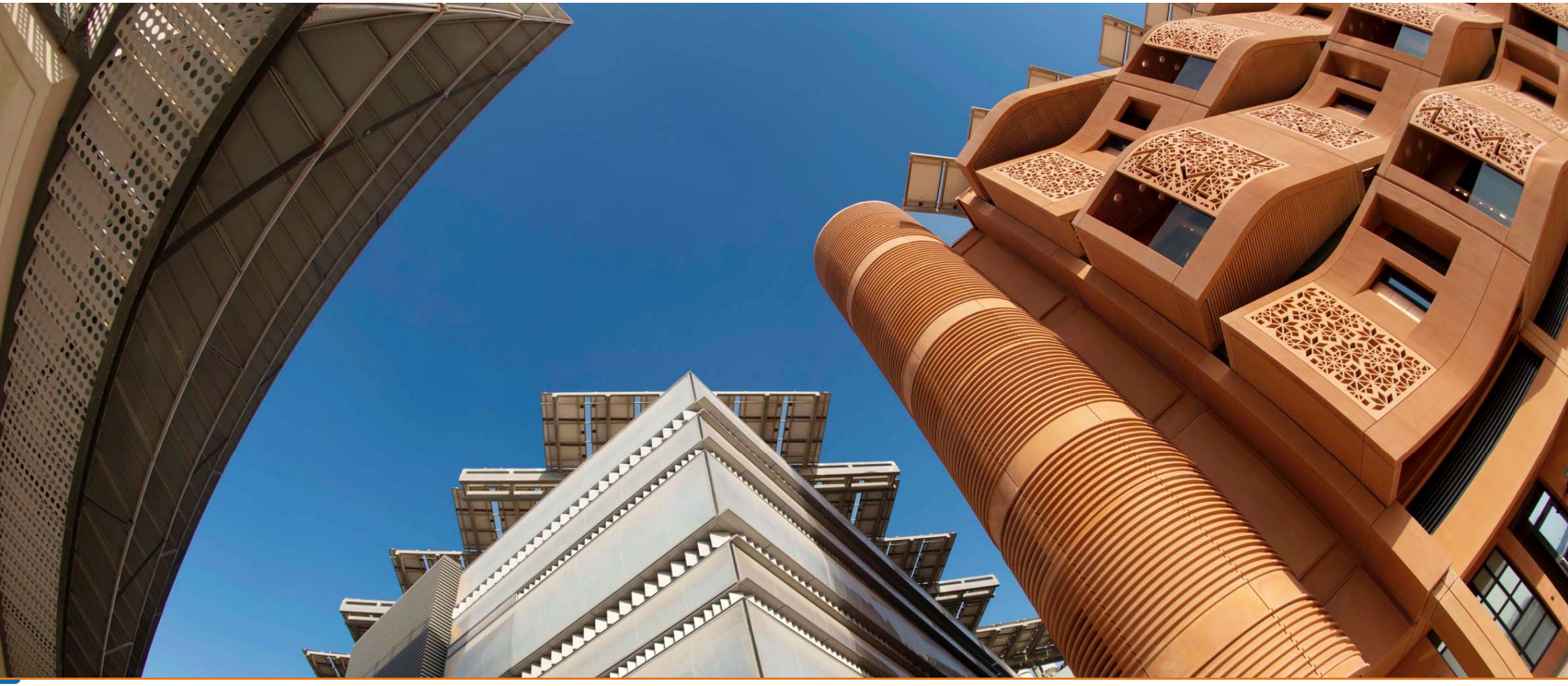


The cold gasification efficiency for the four plastic particles

[1] Skodras, G., Someus, E., Grammelis, P., Palladas, A., Amarantos, P., Basinas, P., Sakellaropoulos, G. P. (2007). Combustion and environmental performance of clean coal end products. International Journal of Energy Research, 31(12), 1237.

Conclusion

1. A comprehensive, predictive kinetics-based CFD model has been developed for the gasification of plastic waste in the drop tube reactor.
2. Initially the devolatalization kinetics of the model is been evaluated following Arrhenius and Coat-Redfern integral methods. These values were in agreement with other literature data of similar feedstocks. The activation energy for each of the PE, PP, and PS were found to be 340, 220, and 320 kJ/mol, respectively with a rate constant that vary between E10 to E22 min^{-1}.
3. There were no significant changes in both temperature and species distribution in these plastics or their combinations and revealing an increasing order in the cold gasification metrics, from polyethylene, polypropylene, and polystyrene to the plastic mixture of 59.03, 62.73, and 73.13% for PE, PP, and PS, respectively while reaching as high as 89% for the co-gasification mixture. As plastic mixture gave the highest CGE which is a favorable result.
4. This implies that there would be no need for the extra cost of sorting the plastic prior to gasification. The plastic wastes can be gasified directly from household wastes.
5. This study has shown the feasibility of gasification of plastic wastes to give high quality syngas (carbon monoxide and hydrogen).
6. The developed model although has been validated for coal, however it is in the process of validation from the drop tube facility at Masdar Institute for plastics feedstocks.



Thank You