

TECHNOECONOMIC EVALUATION OF PRODUCING HYDROGEN
AND METHANOL FROM WASTE PLASTICS WITH THE CONTROLE
ON GREENHOUSE GAS EMISSIONS

BY

Ali Abdullah Al-Qadri

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

Chemical Engineering

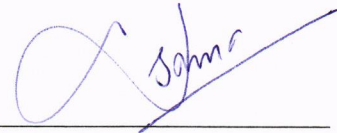
April 2022

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

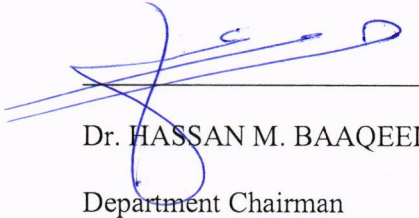
DEANSHIP OF GRADUATE STUDIES

This thesis, written by **ALI AL-QADRI** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN TELECOMMUNICATION ENGINEERING**.

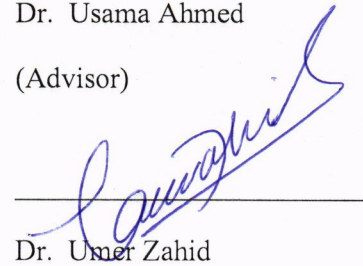


Dr. Usama Ahmed

(Advisor)

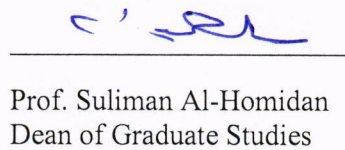


Dr. HASSAN M. BAAQEEL
Department Chairman

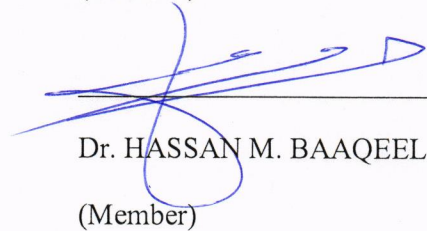


Dr. Umer Zahid

(Member)



Prof. Suliman Al-Homidan
Dean of Graduate Studies



Dr. HASSAN M. BAAQEEL
(Member)

Date



© Ali Abdullah Al-Qadri

2022

[To my mother and my beloved family]

ACKNOWLEDGMENTS

I would like to praise almighty Allah for providing me the knowledge, patience, support, and help for promoting my work successfully. Alhamdulillah who supports me to achieve a good success in my career. All thanks and appreciation to my parents who were very assiduous for pursuing my work efficaciously. My wife always encourages me to be a successful person. My brothers and sisters all of them motivate me to deliver my best performance. I also express thanks to my uncles who supported me during my educational period.

I would like to thank King Fahd University for Petroleum and Minerals (KFUPM) for hosting me during my BS and MS programs. I also would like to thank Chemical engineering department and its faculty and stuffs; it was a great, knowledgeable, and interesting experience with them.

My advisor Dr. Usama Ahmed was great guider and great teacher. He was always available for guidance and support. I also would like to thank Dr. Sagheer Onaizi and my committee members; Dr. Umer Zahid and Dr. Hassan Baaqeel.

My sincere thanks to my friends who were very supportive and motivative; Hamza Abdullah, Monther, Ayman, Yousif, Gubran, Ismail, Anwar, Mohammed Al-Ezi, Mazen, Waheeb, Galal, and all the others. My truthful thanks to Mr. Basheer Abdullah who supported and encouraged me to join the university as a BS student.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES.....	IX
LIST OF FIGURES.....	X
LIST OF ABBREVIATIONS.....	XIII
ABSTRACT	XIV
ملخص الرسالة	XVI
CHAPTER 1 INTRODUCTION.....	1
1.1 Energy Demand and Global Warming	1
1.2 Plastics Global Issues	1
1.3 Studies on Producing Hydrogen and Methanol from Carbonaceous Feedstock	6
1.4 Objectives	9
CHAPTER 2 LITERATURE REVIEW	10
2.1 Hydrogen and Methanol Production Routes	10
2.2 Selection of Plastic Wastes.....	12
2.3 Process for Thermochemical Utilization	14
2.4 Processes in Plastics to Hydrogen and Methanol	17
CHAPTER 3 RESEARCH METHODOLOGY AND PROCESS DEVELOPMENT.....	19
3.1 Modelling and Simulation Approach	19
3.1.1 Design Assumptions and Process Configuration	23

3.1.2 Governing Equations for the Technical Analysis	24
3.1.3 Reaction Kinetics for Methanol Synthesis	27
3.2 Development and Validation of Plastics to Hydrogen Process	29
3.2.1 Sole Hydrogen Production (Case 1-Base Case)	29
3.2.2 Sole Hydrogen Production (Case 2-Alternative Case)	32
3.3 Development and Validation of Case Studies for Dual Hydrogen and Methanol Production	33
3.3.1 Dual Methanol and Hydrogen Production (Case 3-Base Case).....	34
3.3.2 Dual Methanol and Hydrogen Production (Case 4-Alternative Case)	36
CHAPTER 4 RESULTS AND CONCLUSION	38
4.1 Process Performance Analysis and Fuel Production Rates	39
4.1.1 Hydrogen Production Model (Case 1 and Case 2).....	39
4.1.2 Dual Hydrogen and Methanol Production Model (Case 3 and Case 4).....	42
4.2 Syngas Composition Analysis.....	45
4.2.1 Syngas Composition at WGS Outlet for Case 1 and Case 2	45
4.2.2 Composition of Syngas at the Inlet of Methanol Reactor for Case 3 and Case 4	46
4.3 CO ₂ Specific Emissions	49
4.3.1 Analysis of CO ₂ Emissions from Case 1 and Case 2	49
4.3.2 Analysis of CO ₂ Emissions from Case 3 and Case 4	50
4.4 Sensitivity Analysis	51
4.4.1 Analysis of Case 1 and Case 2	51
4.4.2 Analysis for Case 3 and Case 4	63
4.5 Economic Analysis	71
4.5.1 Hydrogen Production Model (Case 1 and Case 2).....	71
4.5.2 Dual Hydrogen and Methanol Production Model (Case 3 and Case 4).....	78
4.6 Conclusion.....	84

REFERENCES.....	86
APPENDICES	102
Appendix A: ASPEN plus Diagram for the Dual H ₂ and CH ₃ OH Production Models	102
A1: The Base Case for Dual Hydrogen and Methanol production (Case 3)	102
A2. The Alternative Case for Dual Hydrogen and Methanol production (Case 4)	106
Appendix B: Kinetics Keyed to the ASPEN Interphase	108
VITAE	115

LIST OF TABLES

Table 1 Literature review for the various possible plastic feed stock with detailed characteristics	13
Table 2 The processes in chemo-thermal utilization of plastics	15
Table 3 The chemical processing units, and their specifications in the literature to process the plastic feed stock.	17
Table 4 Main features in the processes involved in chemical recycling of waste plastics to clean fuels and chemicals	18
Table 5 Plastics and natural gas compositions.....	21
Table 6 Main reactions involved in the processes	22
Table 7 Design Assumptions for the two cases in producing hydrogen and methanol	24
Table 8 Main parameters calculation based on the literature	26
Table 9 The main reactions and the reaction rate expression	27
Table 10 Reaction rate constants (Graaf et al 1989).....	28
Table 11 Adsorption equilibrium constants (Graaf et al 1989)	28
Table 12 Reaction equilibrium constants (Graaf et al 1986)	28
Table 13 PP model validation for the gasification process at 800 °C and a mass ratio S/F of 2.....	32
Table 14 PE model validation for the gasification process at 900 °C at a molar ratio of 2 (i.e., mass ratio of 188 to 100).....	32
Table 15 Outlet flowrates of each process at each unit and stream composition	40
Table 16 Comparison between the two designed models in terms of energy calculation	41
Table 17 Mainstream specifications and the unit outlet results.....	43
Table 18 The major evaluated parameters representing the energy analysis for the two cases.....	44
Table 19 Economic assumptions	72
Table 20 CAPEX cost summary for the two studied cases for hydrogen production	74
Table 21 OPEX cost summary for the two modeled cases: hydrogen production	75
Table 22 The capital expenditures cost summary for hydrogen and methanol production	79
Table 23 The operating expenditures summary for the two cases for hydrogen and methanol production	80
Table 24 Kinetic factors and driving forces parameters inputted to the ASPEN interphase	108
Table 25 Adsorption constants inputted to the ASPEN interphase	109

LIST OF FIGURES

Figure 1 The main hydrogen production routes.....	11
Figure 2 The main methanol production routes.....	12
Figure 3 The general routes of chemical production from recycled wasted plastics.....	14
Figure 4 The base flow diagram of plastic wastes to clean fuels through pyrolysis	18
Figure 5 Producing hydrogen and methanol from waste plastics via conventional method (i.e., case 1).....	30
Figure 6 Producing hydrogen and methanol from waste plastics via integrated model with SMR process (i.e., case 2)	33
Figure 7 Producing hydrogen and methanol from waste plastics via conventional method (i.e., case 1).....	35
Figure 8 Producing hydrogen and methanol from waste plastics via integrated model with SMR process (i.e., case 2)	37
Figure 9 Comparison between base model and methane reforming model in terms of outlet syngas composition after WGS unit	45
Figure 10 Comparison between base case and methane reforming models in terms of the total process efficiency and molar ratio of hydrogen to carbon monoxide before WGS	46
Figure 11 Comparison between base model and alternative model in terms of syngas composition at the inlet to methanol synthesis process.....	47
Figure 12 The process efficiency and normalized production rate of methanol for case 1 and case 2	48
Figure 13 Comparison between base model and methane reforming model in terms of mass conversion of the feed to hydrogen and in terms of CO ₂ specific emissions (CSE)	50
Figure 14 Comparison case 1 and case 2 in terms of CO ₂ specific emissions (CSE) and normalized hydrogen production rate (HPF).....	51
Figure 15 Scheme diagram for the plastic gasification process.....	52
Figure 16 An equal blend of PE and PP steam to feed ratio effect on produced moles distribution and LHV at 900 °C	54
Figure 17 An equal blend of PE and PP gasification temperature effect on gases production distribution and LHV at mass ratio of S/P 1	55
Figure 18 Effect of gasification temperature and plastic blend on syngas at steam to feed ratio of 1 (PE/PP mass basis).....	56
Figure 19 Effect of gasification steam to feed ratio and plastic blend on syngas at a gasification temperature 900 °C (PE/PP mass basis).....	58
Figure 20 Scheme diagram for the WGS process	59
Figure 21 The effect of WGS steam inlet to the CO conversion for a mass ratio PE/PP of 0.5; S/F of 1.25	60

Figure 22 Effect of first WGS cooling duty on the conversion of carbon monoxide conversion for a mass ratio PE/PP of 0.5; S/F of 1.25	61
Figure 23 Effect of second WGS cooling duty on the conversion of carbon monoxide conversion for a mass ratio PE/PP of 0.5; S/F of 1.25	62
Figure 24 Effect of pressure in gasification and WGS units on the final produced amount of hydrogen.....	63
Figure 25 Impact of plastic gasifier temperature and pressure on the syngas SN ratio...	64
Figure 26 Impact of plastic gasifier temperature and pressure on H ₂ /CO ratio	65
Figure 27 Effect of SMR total mass flow rate on the hydrogen composition and syngas molar flow rate at the inlet of methanol process	66
Figure 28 Impact of SMR total mass flow rate on the final hydrogen production rate per syngas at the inlet to methanol process	67
Figure 29 Effect of SMR total mass flow rate on the final purity of produced hydrogen	67
Figure 30 Impact of SMR total mass flow rate on the production rate of methanol per mixed syngas SN stoichiometric number	69
Figure 31 Impact of methanol reactor temperature on its production rate	70
Figure 32 Impact of methanol reactor pressure on its production rate	70
Figure 33 The TIC per ton and hydrogen cost for the two cases	76
Figure 34 Cash flow diagram for the two cases to produce hydrogen from plastics: base case and methane reforming case.	77
Figure 35 Hydrogen production cost on our study compared with previous studies.....	78
Figure 36 The TIC per ton of methanol and hydrogen for the two cases	81
Figure 37 Cash flow diagram for case 1 and case 2 for methanol and hydrogen production	82
Figure 38 Dual methanol and hydrogen production costs on our study compared with previous studies	83
Figure 39 Steam gasification and H ₂ S removal units in case 1(base case design)	102
Figure 40 Methanol synthesis unit in case 1 (base case design).....	103
Figure 41 WGS unit in case 1 (base case design).....	104
Figure 42 CO ₂ removal unit with the solvent regeneration in case 1 (base case design)	105
Figure 43 Steam gasification and SMR units in case 2 (the alternative case)	106
Figure 44 H ₂ S removal with the solvent regeneration in case 2 (the alternative case)...	107
Figure 45 Methanol synthesis unit in case 2 (the alternative case).....	108
Figure 46 The kinetic factor for CO hydrogenation to methanol	109
Figure 47 The CO hydrogenation driving force plugged to Aspen interphase for the first term	110
Figure 48 The CO hydrogenation driving force plugged to Aspen interphase for the second term.....	110
Figure 49 The kinetic factor for CO ₂ hydrogenation to methanol	111

Figure 50 The CO ₂ hydrogenation driving force plugged to Aspen interphase for the first term.....	111
Figure 51 The CO ₂ hydrogenation driving force plugged to Aspen interphase for the second term.....	112
Figure 52 The kinetic factor for the RWGS reaction.....	112
Figure 53 The RWGS reaction driving force plugged to Aspen interphase for the first term.....	113
Figure 54 The RWGS reaction driving force plugged to Aspen interphase for the second term.....	113
Figure 55 ASPEN Plus interphase for the input of Graaf.et.al kinetics to synthesize methanol using PFR reactor (adsorption expression).....	114

LIST OF ABBREVIATIONS

PE	Polyethylene
PP	Polypropylene
SMR	Steam Methane Reforming
GHG	Greenhouse Gases
LHV:	Lower Heating Value
WGS	Water Gas Shift
CAPEX	Capital Expenditures
OPEX	Operating Expenditures
SN	Stoichiometric Number
PR	Peng Roberson
ER	Equivalence Ratio
CSE	Specific CO ₂ Emissions
HPF	Hydrogen Production Rate per Feedstock Rate
HHV	Higher Heating Value
MeOH	Methanol
AGR	Acid Gas Removal
CEPCI	Chemical Engineering Plant Cost Index
TIC	Total Investment Cost per Ton
SP	Steam to Plastic Ratio

ABSTRACT

Full Name : Ali Abdullah Qasem Al-Qadri
Thesis Title : [Technoeconomic Evaluation of Producing Hydrogen and Methanol from Waste Plastics with the Control on Greenhouse Gas Emissions]
Major Field : [Chemical Engineering]
Date of Degree : [04/2022]

The recent tremendous need for hydrogen as a clean fuel has grabbed the attention to offer alternatives for hydrogen production. Methanol is also considered a very essential chemical for synthesis of several fuels, and chemical products. Plastic wastes are among the alternatives to produce hydrogen and methanol, because of their high heating value, availability, and their drastic impacts to the environment. Polyethylene (PE) and polypropylene (PP) have the highest portion of worldwide produced plastic wastes. Therefore, we produced hydrogen and methanol from plastic wastes (i.e., PE and PP) via steam gasification process using Aspen Plus ® software. The syngas composition from steam gasification was validated with several results from the literature. Our first model (Case 1) is to produce hydrogen from waste plastics. The second model (Case 2) involves steam methane reforming (SMR). In this approach, the syngas at the outlet of plastic gasification is integrated energetically with the SMR inlet feed. Then, the syngas produced from the two processes are mixed and further processed to get pure hydrogen. The third approach (Case 3) is like Case 1; however, syngas is introduced to methanol production unit and the unreacted gases are further processed to produce pure hydrogen (Case 3). The final model is Case 4 which entails the integration of plastic gasification and SMR, however, with the production of methanol. The main processes involved in the study are water gas shift unit (WGS), SMR, methanol production, and acid gas removal (AGR). The

aim of WGS is to maximize the hydrogen production by converting the carbon monoxide to hydrogen and CO₂. Then, Gas cleaning has been implemented to capture CO₂ and H₂S. Extensive sensitivity analysis was conducted seeking the optimal operational conditions. Case 1 is considered as a conventional case in producing hydrogen. Case 2 is the alternative; potentially promising case and it was compared with Case 1. Similarly, Case 3 was assessed with Case 4. The energy and economic analysis were conducted; however, the main key parameters in the study were the GHG emissions, hydrogen production rate, overall energy efficiency, and fuel production cost. The implementation of Case 2 enhanced the hydrogen production rate by 5.6%. Additionally, the overall process efficiency was improved by 6.43%. The CO₂ specific emissions were reduced by 1.0%. Ultimately, the hydrogen lifetime production cost was reduced by 29%. On the other hand, the results from Case 4 were promising than Case 3. Thoroughly, the overall process efficiency of Case 4 was higher than Case 3 by 9.0%. The levelized fuel (H₂ and methanol) production cost was improved in Case 4 by 51.83%. Therefore, plastic thermochemical recycling via steam gasification coupled with SMR is economically feasible either to produce hydrogen or methanol. Additionally, the integrated case is more convenient than the conventional case because it efficiently utilizes the energy and significantly reduces the fuel production cost.

Keywords: Gasification; Reforming; Waste Plastic; Methanol production; GHG Emissions

ملخص الرسالة

الاسم الكامل: علي عبد الله قاسم محمد القادري

عنوان الرسالة: التقييم التقني الاقتصادي لإنتاج مركبي الهيدروجين والميثانول من البلاستيك المستخدم مع مراعاة السيطرة على انبعاثات ثاني أكسيد الكربون

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: 04/2022

الطلاب الهائل المتزايد على الهيدروجين كوقود نظيف لفت الأنظار بقوة للبحث عن بدائل لإنتاجه. إضافة إلى الأهمية الكبرى للهيدروجين أيضا الميثانول يعد واحدا من المركبات الكيميائية الضرورية والتي يمكن من خلالها صناعة مواد عديدة ذات أهمية وقيمة عالية. يعتبر البلاستيك المستخدم بديلا مميّزا لإنتاج الهيدروجين والميثانول لأن البلاستيك موجود بكثرة ويحتوي على مخزون عالي نسبيا من الحرارة ولأن عدم معالجته وإعادة تدويره يتسبب في كوارث للبشرية وللبيئة. بولي اثيلين وبولي بروبيلين يمثلان الأعلى استخداما من بين كل أنواع البلاستيك. لذلك قمنا باختيارهما كممثلين للبلاستيك لعملية التدوير الثير وكيميائية. نستخدم ASPEN PLUS لإثبات فعالية فكرتنا. الدراسة الأولى مثلت الحالة الاعتيادية لإنتاج الهيدروجين والميثانول من البلاستيك واستخدمنا فيها عملية التغويز فقط. من ثم قارنا نتائجنا بنتائج مسجلة في دراسات سابقة وتم التحقق من أن نتائجنا صحيحة مطابقة للواقع. الدراسة الثانية أنتجنا فيها الهيدروجين والميثانول من البلاستيك ومن الغاز الطبيعي بنفس الوقت (دمجنا عمليتين لإنتاج الغاز الاصطناعي وهما عملية التغويز بمساعدة البخار وعملية التهذيب الكيماوي بمساعدة البخار أيضا). الهدف من الدراسة الثانية استغلال كمية الحرارة الكبيرة الناتجة عن عملية التغويز واستخدامها في تسخين الغاز الطبيعي الداخل. في كلا الدراستين نقوم بمعالجة الغاز الاصطناعي وتنقيته من كبريتيد الهيدروجين قبل صناعة الميثانول لأن محفز صناعة الميثانول حساس جدا لكبريتيد الهيدروجين. وبعد صناعة الميثانول نقوم بمعالجة ما بقي من الغاز الاصطناعي بتحويل ما بقي من أول أكسيد الكربون إلى هيدروجين وثاني أكسيد الكربون بالاستعانة بالبخار. وأخيرا نقوم بفصل ثاني أكسيد الكربون عن الهيدروجين باستخدام عملية الامتصاص. بذلك نكون صنعنا الهيدروجين والميثانول بنفس الوقت بدراستين مختلفتين. نفس الأمر طبقناه على الدراستين لكن فقط لصناعة الهيدروجين من دون إضافة عملية صناعة الميثانول لذلك تكون معنا أربع حالات. الحالة 1 من خلالها صنعنا الهيدروجين فقط من البلاستيك عبر عملية التغويز المعالج بالبخار. الحالة 2 دمجنا عمليتي التغويز وعملية التهذيب الكيماوي وأنتجنا الهيدروجين فقط. الحالة 3 أنتجنا الهيدروجين والميثانول بنفس الوقت لكن من البلاستيك فقط. الحالة 4 أنتجنا الهيدروجين والميثانول من البلاستيك ومن الغاز الطبيعي بنفس الوقت. قمنا بمراعاة السيطرة على كمية ثاني أكسيد الكربون المنتجة والتحكم فيها وكانت أقل في الحالة 2 والحالة 4 مقارنة ب 1 و 3. أيضا الكفاءة العملية كانت أعلى في الحالة 2 والحالة 4 عن الحالتين 1 و 3 بمقدار 1.82 و 12.75 % تواليًا. بالنسبة للتحليل الاقتصادي أظهرت الحالتين 2 و 4 تفوقا على الحالتين 1 و 3 في سعر إنتاج الوقود بمقدار 29 و 51.83 % تواليًا. بالإضافة إلى ذلك إنتاج الوقود في الدراسة الثانية كان أكثر. الدراسة الثانية أيضا مثلت تطورا كبيرا في الكفاءة من الناحية الإنتاجية والاقتصادية ومن ناحية تقنين استخدام الطاقة. لذلك ننصح بتطبيق الدراسة الثانية سواء لإنتاج الهيدروجين وحيدا أو لإنتاج الميثانول والهيدروجين معا. بالإمكان الإضافة على دراستنا باستخدام نموذج يقوم بصناعة الايثانول بنفس الطريقة.

CHAPTER 1

INTRODUCTION

1.1 Energy Demand and Global Warming

The global demand of energy has considerably enlarged during the last few decades because of fast industrialization, population increase, and transportation. The forecasted energy demand by Global Energy Outlook for the next two decades is 30 % increase [1]. Nevertheless, the conventional processes produce appreciable amount of CO₂. Therefore, increasing the utilization of those processes increases the carbon dioxide emissions up to 415 ppm which would drastically affect human health and cause climate change and global warming. The Paris climate change conference was stated that, the global rise temperature should be controlled below 2 °C till 2050[2]. It could be achieved by enhancing the efficiency of processes and by developing alternative processes that limit the CO₂ emissions [3] [4]. Consequently, accomplishing alternative processes to produce energy with the control of carbon dioxide emissions is crucial. One of the alternatives is to utilize the plastic wastes to produce valuable products.

1.2 Plastics Global Issues

Globally, the portion of plastics recycled from 1950-2018 is just 9% out of 6.3 billion tons. Additionally, 12% had been burnt [5]. However, the remaining 79% of plastics contributes in severe harmful pollutants. Those pollutants have different forms such as

Furans, Dioxins, and Mercury. The pollutants are highly hazardous causing climate changes, and negatively affecting the environment and marine lives [6][7]. Moreover, 4-12 million tons of plastics are through to the ocean annually [8]. Hence, many countries encouraged recycling the plastics and they established associated regulations [9]. Therefore, efficient recycling of plastics to valuable products is essential to save the environment and to utilize this huge waste. Several studies confirmed the feasibility of plastic recycling [10]–[12].

The recycling process involves four main steps, which are collection, separation, manufacture, and marketing [13]. Industrial recycle could be through the direct reuse of the plastics, mechanical treatment, or chemical processing (using them as feed stocks for various chemical applications) [14]. The most convenient technique in plastic recycling is the chemical processing due to the change of plastic properties in the first use [15]–[17]. The chemical processing of plastics is classified as a tertiary thermo-chemical recycle, which could be through chemolysis (homogeneous), or cracking, and gasification (heterogeneous) [18]. The cracking could be thermal or catalytic or both simultaneously. The chemo-thermal recycling of plastics is one of the applicable technologies because it surely produces synthesis gas which could be used in synthesizing several valuable chemicals.

Gasification is a process that produces carbon-based gases (CO_2 , CO), and hydrogen from the conversion of carbon-based materials such as fossil fuels, and biomass [19]. The product achieved through a high temperature reaction ($> 700^\circ\text{C}$) using oxygen or steam as an auxiliary component (air gasification or steam gasification) for process enhancement without combustion [20]–[23]. Steam gasification, air gasification, co-

gasification, pyrolysis, and plasma gasification are types of the thermal recycling of the plastics or any carbon-based feedstock [24]. Pyrolysis is a dry heating of the feed in the absence of air [25]. Several studies had investigated the thermal processing of plastics via pyrolysis [26]–[31]. Although, the pyrolysis produces syngas completely free of tar [32], however, the hydrogen to carbon monoxide ratio is less. Sometimes, it is considered as the first step in the gasification process because it maximizes the conversion of volatile materials (high carbon chain) to a relatively low carbon hydrocarbons ($<C_{25}$) [33]–[36]. Another process is co-gasification which is the mix of plastic feed stock with coal or biomass to enhance the gas yield and suppress char formation [37]. However, this process increases the tar formation [38]. Air gasification produces lower tars, nevertheless, it produces lower hydrogen to carbon monoxide ratio [39]. Pure oxygen gasification is a very efficient process among the others, however, the production of oxygen from air is highly expensive [40]. To effectively produce syngas with high H_2/CO ratio in a quite simple process, steam gasification of plastics is the optimal option [41].

Production of syngas facilitates the production of energy, and very crucial clean fuels, such as hydrogen, methanol, ethanol, DME, LPG, olefins, and gasoline [42]–[44]. Modeling the whole journey of plastics to clean fuels under several operational conditions is essential to support the industrial applications, and to maximize the clean fuel production from a heterogeneous plastic mixture [45]–[48]. A study conducted by Antzela, and Ioanna (2018) [49], for the techno economic evaluation of simulation of pilot plant about the conversion of plastics into heavy oil through pyrolysis using Aspen HYSYS. The production cost of the produced heavy oil was £0.87/kg which is 58%

higher than the market price. Thus, they suggest a more sophisticated study for a large-scale data. Na Deng et al. 2018[50], modeled the municipal solid plastic (MSW) to syngas using combined two technologies: pyrolysis (RYield+ RGibbs), and gasification (RGibbs). Their results showed good agreement with the experimental data, where they elected 750 °C as the optimal gasification temperature, and gasifying agent ratio of 0.4. Furthermore, they economically recommended the use of flue gas and steam as gasifying agents. Another study done by Pravin et.al (2012) [51], about the conversion of PE (polyethylene) to syngas through pyrolysis then gasification using Aspen plus. The results were not validated with an experimental one due to the lack of resources, however, they claimed the most convenient temperature, and equivalence ratio (ER; steam to fuel ratio) for the pyrolysis unit, which were 0.4-0.6, and 500-750°C.

Hydrogen has several appealing characteristics such as high energy conversion, renewable production, zero emissions, reliability, wide sources, and large storage capacity [52][53]. It is considered the cleanest fuel in this century. Hydrogen receives great global attentions because it is a raw material for wide industrial processes such as ammonia synthesis, water gas shift, and petroleum refinery. The main production pathway of hydrogen is from traditional fossil sources with 96% (48 % from natural gas, 30% from naphtha reforming, and 18% from coal gasification) [54]. Therefore, investigating other alternatives (such as wastes utilization) to produce H₂ is essential. The second crucial industrial chemical is methanol. Methanol has great and varied industrial applications. It is used as a raw material to produce DME, formaldehyde, acetic acid, and MTBE [55]. Additionally, there is a growing trend to be blended with

gasoline to enhance the fuel octane number and other properties. It is also used as a direct fuel in methanol fuel cell [56]. Moreover, it is utilized in producing olefins and polymers via MTO, then polymerization processes [57]. Thus, hydrogen and methanol are very crucial fuels, and they need to be abundant to meet the industrial growth via alternative technologies. The most promising technology is to utilize the waste plastics as stated.

Fivga, and Dimitriou [58], studied the waste plastics to heavy fuel with techno economic evaluation. They used a mixed feed of PE, PP, and PS at 530°C, and 1 atm. They modeled their work using Aspen HYSYS based on ultimate analysis of the plastics. The product of their pyrolysis reactor is basically n-C30, n-C25, n-C18, n-C14, n-Octane, ethane, and small portion of gases. The remaining solids and gases are separated then, pyrolysis liquid fuel is collected. They validated their results with plant data, and they did some cost analysis. Generally, the work is promising and has the idea of plastic waste to liquid heavy fuel. Another study on plastic waste conversion to fuel was conducted by Emad and Vahid [59], which basically on production of hydrogen fuel via co-gasification of a mix feed of asphaltene and plastics using Aspen Plus. They decomposed the feed on a pyrolysis reactor (RYield), then they used RGibbs reactor followed by CSTR to produce syngas. They studied some factors influencing the hydrogen production rate which namely are asphaltene to plastic ratio (A/P), equivalence ration (ER), and steam to feed ratio (S/F). They found that A/P, and S/F have a positive impact on carbon conversion efficiency (CCE). The study provided an excellent idea on producing hydrogen from a co-gasification mixture. However, they did not produce a pure hydrogen; it was a synthesis gas mixed with acid gases which

need to be removed. Additionally, they need to implement WGS to maximize hydrogen production and to suppress the carbon monoxide in the product.

1.3 Studies on Producing Hydrogen and Methanol from Carbonaceous Feedstock

There are limited studies on the production of hydrogen from plastic wastes. Hence, investigating the hydrogen production from different feedstock (i.e., coal or biomass) will support on producing hydrogen from plastics. A study performed by AlNoussa et al. [60], on techno economic evaluation of producing H_2 from biomass. They investigated different gasifier agents and the type of several types of feedstocks. They found that, steam as gasification agent was better than other agents. Namioka et al. [61], studied the production of synthesis gas with higher hydrogen content using pyrolysis, then low temperature steam gasification. They investigated polystyrene (PS), and polyethylene (PE). They performed the pyrolysis, and steam reforming at 673 and 903 K respectively. Ruthenium was used as a pyrolysis catalyst, and it enhanced the process performance. The study recommended combining the thermal and catalytic process. Another study accomplished by Chaia et al. [62], on the conversion of plastics to hydrogen using a combination of co-pyrolysis and gasification process. A Ni-CaO-C was tested as a novel catalyst to promote H_2 production. They claimed effective production of hydrogen with an 87.7 mole% controlling the greenhouse gases. Consequently, the conversion of waste plastics into hydrogen is a practical process proved theoretically and experimentally. Although, the use of the catalysts in a gasification process is energetically superior, however, it is more complex and requires more development. Thus, we will accomplish our work using steam gasification which was recommended by AlNoussa et al. [61].

There are limited studies on the thermal conversion of plastic wastes to hydrogen and methanol. Acomb et al. (2013) studied the production of hydrogen from plastics taken from waste electronic equipment via pyrolysis-gasification in two different stages [63]. The plastics were first pyrolyzed in the first stage at 500 °C, then, they were fed to the second stage (i.e., steam gasification reactor) at 800 °C. They stated that, increasing the steam to plastic ratio enhance the hydrogen production. Additionally, they claimed that, using two stages (pyrolysis then gasification) enhances the hydrogen production from plastic electronic wastes. Another study on production of hydrogen using the two thermos-chemical stages was conducted by Chunfei and Williams (2010) [64], using several plastics (polypropylene, polystyrene, and high-density polyethylene). Higher gaseous yields were perceived for HDPE and PP compared to PS (53.5, 59.6, and 11.2 % respectively). Namioka et al. (2011), studied the production of hydrogen rich gas from waste plastic (polystyrene) via pyrolysis, then steam reforming. Their results retrieved that, optimal gas production (60 g/h) with minimum coke fractions were achieved at pyrolizer temperature of 400 °C, with steam reforming temperature of 630 °C [65]. Takafumi et al. (2002) [66], conducted a study on producing methanol via partial oxidation of waste plastic (polyvinyl chloride). They made a demonstration plant feeding 5 tons of plastic per day; producing syngas via entrained single stage reactor. Then, methanol was synthesized via liquid phase catalytic process. They were successful in producing methanol with 98% purity with a conversion and gas cold efficiency of 96% and 63% respectively. There is a lack in the complete, detailed studies on the conversion of plastics to hydrogen and methanol. However, there are certain studies on dual production of hydrogen and methanol from coal and biomass.

The thermochemical recycling route of plastics to hydrogen and methanol is pretty like that one for coal with the variation in the feed composition which results in using different operational conditions and slightly different design. A study delivered by Usama et al. (2021) using Aspen Plus, in coproduction of H_2 and methanol using a mix fuel of coal and biomass [67]. They developed a novel design that incorporates the steam methane reforming process with the coal-biomass gasification process. They stated a reduction in the specific energy requirement by 29% and an enhancement in the process efficiency by 3.5% when the novel design was used. They performed the techno economic evaluation for the two designs and perceived a 7.3% reduction in the total fuel cost. Another dual study was performed by Usama Ahmed (2021) on the production of H_2 and methanol from coal on two cases. The base case was the normal gasification process to produce syngas, then the syngas was catalytically converted to methanol and the remaining gas was processed via water gas shift to hydrogen. On the other hand, the alternative case was an integrating design with steam methane reforming process (SMR) process to utilize the high temperature stream from the gasifier. The results revealed that, the alternative case had higher process efficiency by 4.28% with 18.3 % reduction in the specific energy requirement. Additionally, the alternative case offered a reduction in fuel production cost by 13%. Moreover, the specific carbon dioxide emissions were lower in the alternative case by 34.3% [68]. Those studies proved the feasibility and the efficiency of the co-production of hydrogen and methanol from a carbon-based feedstock. However, the dual production system from plastics has not been investigated.

1.4 Objectives

Our objective is to simulate the waste plastics (i.e., polyethylene and polypropylene) to clean fuel (i.e., hydrogen and methanol) through Aspen plus, then we will perform a technoeconomic evaluation of two different cases. The first case will be the conventional technology in producing syngas through gasification, then through syngas processing, the hydrogen production rate will be maximized. Finally, the acid gases will be removed via AGR unit. The second case will be via integrating steam methane reforming (SMR) with steam gasification to maximize the syngas production, improve the quality and to enhance the energy utilization and reduce the overall production cost. For both cases, steam gasification of waste plastics to syngas will be validated with experimental data to ensure the model legitimacy. Additionally, sensitivity analysis will be conducted to maximize the production, and optimize the operational parameters. Furthermore, we will ensure controlling of greenhouse gases (i.e., carbon dioxide) and it will be part of comparison between the two cases. Methanol will be produced from syngas, then, the remaining syngas will be fed to WGS unit to convert CO to hydrogen, then it will be cleaned via AGR unit. In summary, we will design a model that produces hydrogen and methanol from PE and PP. Two cases will be simulated (i.e., case 1, and case 2), evaluated, and compared in terms of energy consumption, CO₂ control, and cost analysis. We call four cases; case 1 is the conventional process producing hydrogen from PE and PP. Case 2 represents the integrated model producing hydrogen from plastics via steam gasification and from natural gas via SMR process. Case 3 and case 4 are like case 1 and case 2 respectively, however, methanol process is involved producing hydrogen and methanol likewise.

CHAPTER 2

LITERATURE REVIEW

This section will highlight the production routes of both hydrogen and methanol, then, it will illustrate some collected data about the plastic wastes. After that, it will summarize the main processes available for plastic chemical utilization. Finally, it will explain and demonstrate the processes involved in synthesizing clean fuel from plastic wastes.

2.1 Hydrogen and Methanol Production Routes

Hydrogen is considered as a clean fuel; however, it is produced from several routes; some are renewable, and no carbon emissions and the majority are the classical CO₂ producing routes. Natural gas produces via steam reforming produces hydrogen with the highest process efficiency of 89%. It is the most convenient and producible process. Coal, biomass, and other carbon-based feedstock can produce hydrogen via thermal or catalytic routes. They produce high carbon dioxide emissions; however, biomass and plastics are considered among the renewable resources in producing hydrogen and other chemicals. Additionally, biogas is a renewable resource of hydrogen, since it utilizes the food waste to produce valuable fuels via reforming process. The cleanest process in producing hydrogen is the water electrolysis, however, it is an emerging technology and in most cases is not feasible. **Figure 1** shows the main routes in producing hydrogen from the feed illustrating the path process with the process efficiency. [69]

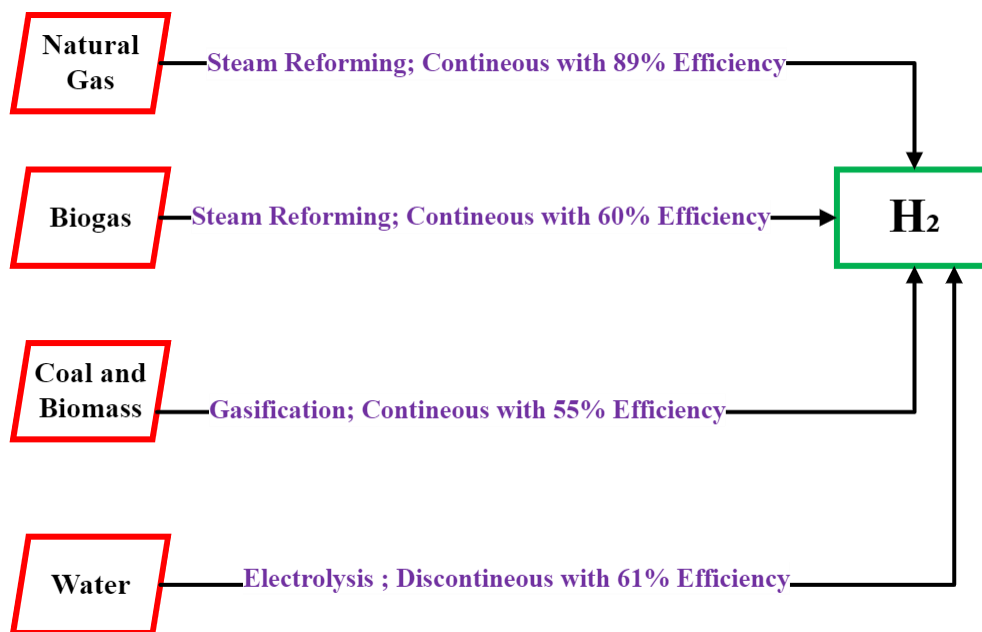


Figure 1 The main hydrogen production routes

Methanol is one of the most valuable chemicals because it could be used as a fuel or to produce other chemicals such as acetic acid and formaldehyde. There are several routes in synthesizing methanol. The classical route that produces most of the methanol is the methane (i.e., natural gas) conversion to syngas via steam reforming, then via catalytic process, methanol produced. The natural gas could be directly converted to methanol via methane partial oxidation. It requires pure hydrogen for the efficient process conversion. Syngas could be produced from other resources that ultimately contains carbon such as coal, biomass, and plastics. The synthetic gas produced from methane has higher hydrogen to carbon monoxide ratio. Therefore, it is more efficient. However, plastics are considered as an alternative technology in producing syngas because the plastic wastes are available, and the expected H₂/CO is higher than that when coal is used (plastics have higher heating value). The technically different route producing methanol is the CO₂ hydrogenation to methanol via catalytic process which is considered as a growing and emerging technology.

Figure 2 illustrates the main paths producing methanol with the corresponding process.

[70]

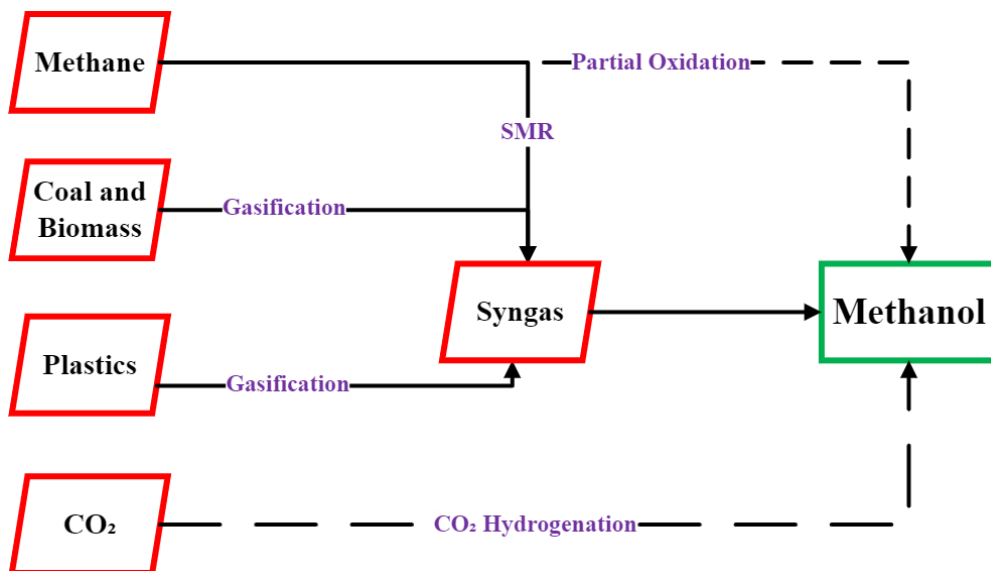


Figure 2 The main methanol production routes

2.2 Selection of Plastic Wastes

There are different kinds of plastics, and hence, various types of plastic waste. Therefore, we wanted to select the one with the highest portion on the global consumption. Additionally, specific properties of the plastics are needed to accurately solve the model.

shows the global demand and consumption of several kinds of plastics, and ultimate, proximate analysis and heating value of those plastics. Polyethylene (PE) and polypropylene (PP) have the highest global consumption; hence, they have been selected for thermal recycling to hydrogen and probably methanol. Additionally, PE and PP have high heating value compared to other plastics.

Table 1 Literature review for the various possible plastic feed stock with detailed characteristics

Characteristics/Types of Plastics	Ultimate Analysis (wt %)					Proximate Analysis (wt %)					HHV (MJ/Kg)	LHV (MJ/Kg)	Annual Global Demand, 2018 (million tons)	Global Consumption (%)	Reference
PE	C	H	N	S	O	Moisture	VM	FC	Ash		42.9	44.15	100	33.5	[146][147]
	85.81	13.86	0.12	0.06	0	0.02	99.85	0	0.15			[145]			
PP	C	H	N	S	O	Moisture	VM	FC	Ash		43.4	46.5	61.87	19.5	[148]
	85.88	14.47	0	0	0	0	99.67	0.10	0.21			[145]			
PET						Moisture	VM	FC	Ash		10.1–13.2	0	18.83	5.5	[149]
						0.7	89	10.2	0.1						
LDPE	C	H	N	S	O	Moisture	VM	FC	Ash		41.742		45.73		[150]
	85.58	14.43	0.01	0	0	0.06	97.81	0.93	1.2						
HDPE	C	H	N	S	O	Moisture	VM	FC	Ash		40.614		40.35		[151]
	85.49	14.52	0	0	0	0.09	98.12	0.97	0.82						
PVC												24.07	43.04	16.5	
PS	C	H	N	S	O	Moisture	VM	FC	Ash		41.7	40.186	18.83	8.5	
	92.20	7.93	0	0	0	0	99.72	0.12	0.16						
Scrap Tyre	C	H	N	S	O	Moisture	VM	FC	Ash		38.5		1.5		[152]–[154]
	85.2	7.3	0.4	2.3	0.5	1.2	61.3	33.5	5.2				billion* tyres		

2.3 Process for Thermochemical Utilization

The first step in chemical conversion of waste plastics is the decomposition to its ultimate composition. Then, via gasification, syngas will be produced with some of greenhouse gases. There are several processes used in the literature which are illustrated in **Figure 3**. Scheme of the main paths for chemical valorization of waste plastics[25]. Steam gasification is a great option to produce hydrogen or syngas. Although, steam gasification requires high energy (i.e., endothermic process), however, it is relatively simple and provides a high H_2/CO in the produced syngas[41]. The comparison between the plastic valorization processes is given in **Table 2**.

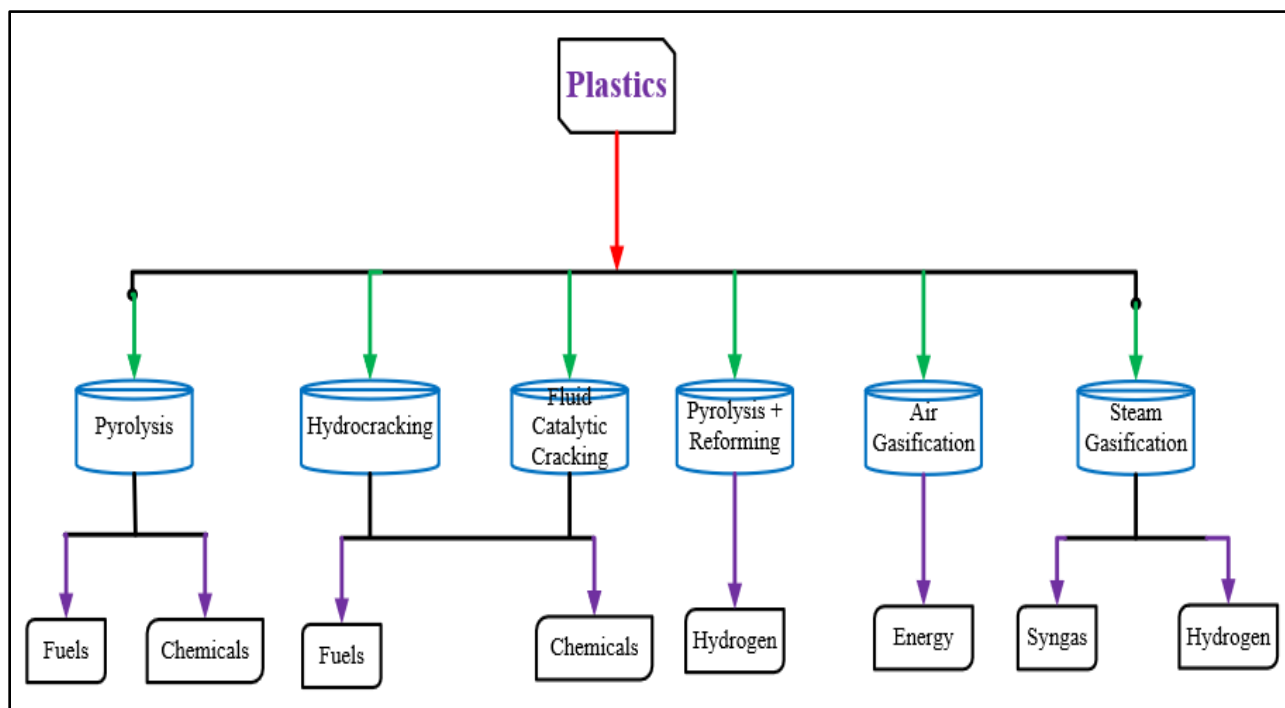


Figure 3 The general routes of thermochemical utilization of waste plastics (i.e., production of syngas)

Table 2 The processes in chemo-thermal utilization of plastics

Valorization process	Features	Advantages	Disadvantages
Air gasification	Using air as a gasifying agent	✓ Simplicity of the process ✓ No external energy requirement ✓ The tar content is relatively low[39].	➤ Low H ₂ /CO ratio
Steam gasification	Using steam as a gasifying agent	✓ High H₂/CO ratio	➤ Endothermic steam reforming reactions required higher energy[41].
Pure O₂ gasification	Using pure O ₂ instead of air	✓ Combines the advantages of air and steam gasification[40].	➤ The O ₂ separation from air is complex and expensive
Co-gasification	Mixing plastic feed stock with coal or biomass	✓ Enhances gas yield and H₂ production and lowers char[37]. ✓ Provides interesting synergistic behavior due to the positive interaction between polymer degradation and biomass chars[71]–[74]. ✓ Minimizes problems related to feeding.[75]	➤ Increase tar formation[38]
Pyrolysis	Heating in the absence of air	✓ It has been proposed and guaranteed by several studies and researchers[26]–[31]. ✓ It takes advantage of reforming catalyst, thus, syngas completely free of tar could be produced[32].	

Herein, we report some studies about production of syngas from waste plastics using various techniques. The survey summary is given in **Table 3** which illustrates the process specifications and the resulted hydrogen to carbon monoxide on the produced syngas. Fivga, Dimitriou (2018)[58], studied the waste plastics to heavy fuel with technoeconomic evaluation. They used a mixed feed of PE, PP, and PS at 530 °C, and 1 atm. They modeled their work using Aspen HYSYS based on ultimate analysis of the plastics. The product of

their pyrolysis reactor is basically n-C30, n-C25, n-C18, n-C14, n-Octane, ethane, and small portion of gases. The remaining solids and gases are separated then, pyrolysis liquid fuel is collected. They validated their results with plant data, and they did some cost analysis. Generally, the work is promising and has the idea of plastic waste to liquid heavy fuel.

Another study on plastic waste conversion to fuel was conducted by Emad and Vahid (2018)[59], which basically on production of hydrogen fuel via co-gasification of a mix feed of asphaltene and plastics using Aspen Plus. They decomposed the feed on a pyrolysis reactor (RYield), then they used RGibbs reactor followed by CSTR to produce syngas. They studied some factors influencing the hydrogen production rate which namely are asphaltene to plastic ratio (A/P), equivalence ration (ER), and steam to feed ratio (S/F). They found that A/P, and S/F have a positive impact on carbon conversion efficiency (CCE). The study provided an excellent idea on producing hydrogen from a co-gasification mixture. However, they did not produce a pure hydrogen; it is a synthesis gas mixed with acid gases which need to be removed. Additionally, they need to implement WGS to maximize hydrogen production and to suppress the carbon monoxide in the product.

The previous studies gave a sufficient data to start simulating plastics to hydrogen, especially, the decomposition and gasification steps (i.e., **Table 3**). The other studies are discussed later in this report.

Table 3 The chemical processing units, and their specifications in the literature to process the plastic feed stock.

Process	Reactor	Plastic Type	Oxidant to Plastic Ratio	T (°C), P (atm)	Analysis Type	H ₂ /CO	Ref.
Pyrolysis	RYIELD	PE	0.2	727, 1	Ultimate	1.4	[76]
Steam Gasification	RYIELD	PE	S/F (steam to Fuel) = 1	900, 1	Ultimate	2.1	[77]
Co-gasification	RYIELD	Asphaltene Plastics	0.8 & S/F = 0.2	850, 1	Ultimate	0.42	[59]
Pyrolysis		PE + PP + PS		530, 1	Ultimate		[78]

2.4 Processes in Plastics to Hydrogen and Methanol

The raw plastic waste will be decomposed first, then via steam gasification, syngas with relatively higher hydrogen to carbon monoxide ratio will be produced. Then, the gas was quenched by cooling to 250 °C. After that, to maximize hydrogen production, the gas was fed to WGS (water gas shift). Then, H₂S and CO₂ were separated on acid gas removal (AGR). The waste plastic journey to hydrogen and methanol is illustrated on **Figure 4**. The most popular operational conditions for the main processes involved in producing clean fuel from plastics are summarized in **Table 4**. Other important fuels and chemicals can also be produced from plastics, such as methanol, and others. For methanol synthesis, other routes could be possible depending on the syngas composition. Different plastic wastes could be treated to produce various chemicals and fuels depending on the process path.

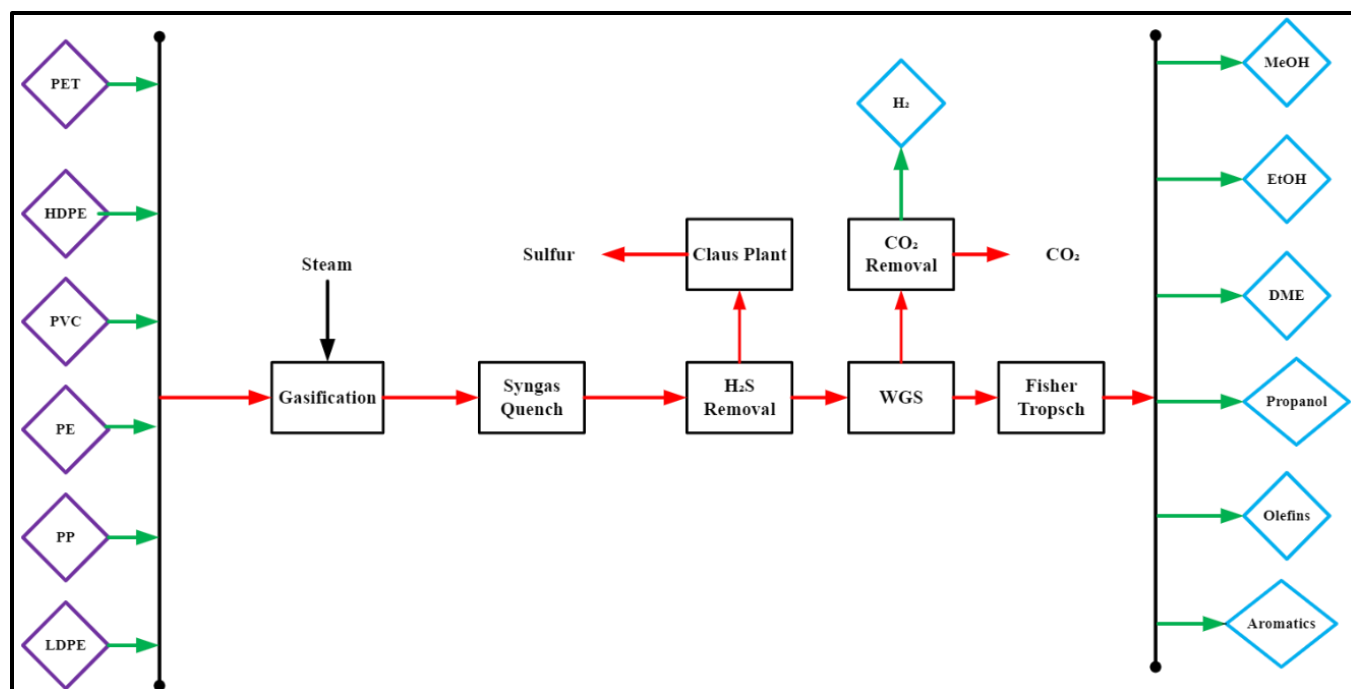


Figure 4 The base flow diagram of plastic wastes to clean fuels through pyrolysis

Table 4 Main features in the processes involved in chemical recycling of waste plastics to clean fuels and chemicals

Process	Definition	Main Reactions	Usual Conditions	Main Products	Ref.
Pyrolysis	Dry decomposition of the waste plastics (thermal cracking).		450 -650 °C	Ultimate analysis of plastics	[79]
Steam Gasification	Formation of gases at high temperature.	$C + H_2O \leftrightarrow CO + H_2$ $C + 2H_2O \rightarrow CO_2 + 2H_2$	650-950 °C	Hydrogen, CO, CO ₂ , H ₂ S, H ₂ O	[80]
WGS	Conversion of CO to CO ₂ and H ₂ .	$CO + H_2O \leftrightarrow H_2 + CO_2$	250-450 °C	Hydrogen, CO ₂	[81]
AGR	Cleaning the syngas by removing H ₂ S and CO ₂ .	Physical process	Usually at cryogenic temperature (-30 °C)	Clean hydrogen of chemicals (i.e., free of CO ₂ and H ₂ S)	[82]
Fisher Tropesh	The process of producing chemicals from syngas.	$(2n + 1) H_2 + n CO \rightarrow C_n H_{2n} + 2 + n H_2O$	150-300°C & 20-40 bars	Could be methanol, ethanol, DME, gasoline, aromatics, or LPG	[83]

CHAPTER 3

Research Methodology and Process Development

3.1 Modelling and Simulation Approach

In this study, Aspen Plus was used as a simulation tool choosing Peng Roberson (PR) as a suitable property package. It is commonly indorsed for gas systems and it has wide-ranging of pressure and temperature [84]. Additionally, it has been used by several gasification and reforming studies [85]–[89]. The feedstock composition for the waste plastics (PE and PP) is given in **Table 5**. The global consumption of Polyethylene (PE) and polypropylene (PP) are 33.5% and 19.5% respectively [90]. Additionally, PE and PP have high heating value. Hence, they had been chosen to be recycled in our study. We selected HCOALGEN models to specify the plastics heating value. The plastics were first decomposed in two separate decomposition reactors at a temperature of 650°C. Then, through the steam gasification reactor, syngas was produced with traces of H₂S. In the model, we used RYield reactor in the decomposition step (the yield was the ultimate analysis), and RGibbs reactor to model the gasification step. The gasifier temperature and pressure were selected based on sensitivity analysis to meet the specifications for the next process. To remove the H₂S traces not to affect the methanol catalyst; we inject H₂S removal unit after the gasification unit using lean as an absorbent. The outlet gases were introduced to methanol synthesis unit controlling the inlet operational conditions. Three reactions were involved in methanol synthesis which were CO hydrogenation, CO₂ hydrogenation, and water gas shift. Using a recycle stream, the methanol production was maximized. The uncovered gases were separated and processed in a later process (i.e., WGS) to convert the remaining CO to hydrogen and CO₂ in two REquil reactors connected in series. After that, the gas mixture

was cleaned from CO₂ in AGR (acid gas removal), and finally, the pure hydrogen with some unseparated methane was produced. The alternative case was developed such that, the high energy at the outlet of gasifier is utilized to facilitate the SMR process. The SMR process involved reformer, and gasifier. The reactions for methanol synthesis, WGS, and SMR are given in **Table 6**. The plastic feedstock, the natural gas and steam for gasification and reforming were specified based on selectivity analysis to ensure the syngas high heating value with a proper utilize of energy.

Table 5 Plastics and natural gas compositions

Plastic Composition Analysis		
Proximate Analysis (Weight %)		
	PE	PP
Moisture	0.02	0
Ash	0.15	0.7
Volatile Matter	99.83	99.30
Total	100	100
LHV (MJ/kg)	38.04	44.70
Ultimate Analysis (Weight %)		
Carbon	85.81	86.23
Hydrogen	13.86	12.28
Nitrogen	0.12	0.62
Sulfur	0.06	0.17
Ash	0.15	0.7
Total	100	100
Natural Gas Composition (Mol %)		
CH ₄	93.9	
C ₂ H ₆	3.2	
C ₃ H ₈	0.7	
C ₄ H ₁₀	0.4	
CO ₂	1.0	
N ₂	0.8	
Total	100	
LHV(MJ/kg)	47.76	

Table 6 Main reactions involved in the processes

Gasification Reactor	
$C_{(s)} + H_2O \leftrightarrow CO + H_2$	$\Delta H = + 131 \frac{MJ}{kmol}$
$C_{(s)} + CO_2 \leftrightarrow 2CO$	$\Delta H = + 172 \frac{MJ}{kmol}$
$C_{(s)} + 2H_2 \leftrightarrow CH_4$	$\Delta H = -74.8 \frac{MJ}{kmol}$
$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta H = -41.2 \frac{MJ}{kmol}$
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	$\Delta H = +206 \frac{MJ}{kmol}$
Steam Methane Reforming Reactor	
$3C_2H_6 + H_2O \rightarrow 5CH_4 + CO$	$\Delta H = + 3.6460 \frac{MJ}{kmol}$
$3C_3H_8 + 2H_2O \rightarrow 7CH_4 + 2CO$	$\Delta H = +16.607 \frac{MJ}{kmol}$
$3C_4H_{10} + 3H_2O \rightarrow 9CH_4 + 3CO$	$\Delta H = +41.116 \frac{MJ}{kmol}$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$\Delta H = -802.54 \frac{MJ}{kmol}$
$CH_4 + H_2O \rightarrow CO + 3H_2$	$\Delta H = +206.12 \frac{MJ}{kmol}$
Water Gas Shift Reactor	
$CO + H_2O \leftrightarrow H_2 + CO_2$	$\Delta H = -41.12 \frac{MJ}{kmol}$
Methanol Reactor	
$CO + 2H_2 \leftrightarrow CH_3OH$	$\Delta H = -90.55 \frac{MJ}{kmol}$
$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	$\Delta H = -49.43 \frac{MJ}{kmol}$

$CO_2 + H_2 \leftrightarrow CO + H_2O$	$\Delta H = 41.12 \frac{MJ}{kmol}$
--	------------------------------------

3.1.1 Design Assumptions and Process Configuration

Certain assumptions had been made regarding the operational conditions of the streams and the unit processes. **Table 7** represents the major assumptions taken to simultaneously produce of hydrogen and methanol. The gasification model was constructed based on Dang et al. (2019) [91]. The steam to plastic ratio, and the blend of PE and PP were designated via sensitivity analysis for the gasification process in our previous study for sole hydrogen production. The temperature and pressure of the gasifier was selected such that, the heating value of produced syngas is maximal, and the hydrogen to carbon monoxide ratio is maximized along with the SN ratio. Nickel based catalyst was selected for the reformer unit because its activity and stability were investigated by several studies. Additionally, it ensures high activity and low cost [92]. The WGS catalyst was $\gamma\text{-Al}_2\text{O}_3\text{-}\alpha\text{-Ga}_2\text{O}_3$ oxide investigated by Leon et.al (2020) because it can be active at atmospheric pressure [19]. Then, the AGR unit operational conditions were specified based on Usman et.al (2020) [93]. Rectisol process has been used at two different conditions. Methanol as a solvent was selected because it is produced in the process. The operational conditions were validated with the literature [94].

Table 7 Design Assumptions for the two cases in producing hydrogen and methanol

Equipment	Aspen Model	Assumption
Plastic flowrate	RYield	Plastics = 100 kg/h H ₂ O/ Plastic = 1.25
Gasifier	RYield, RGibbs reactors	Case 1 & 2: Entrained flow gasifier; temperature = 900 °C; P = 1 atm Case 3 & 4: Entrained flow gasifier; temperature = 1500 °C; P = 25 bars
Pre-reformer	RStoic (Reactor)	Heavier hydrocarbon hydrocracking
Reformer	RGibbs (Reactor)	Case 2: Temperature = 894.3 °C, pressure = 3 bar, H ₂ O/NG = 1.6; nickel-based catalyst Case 4: Temperature = 1200 °C, pressure = 25 bar, H ₂ O/ NG (mass basis) = 1.6; nickel-based catalyst
H ₂ S Removal	RadFrac and flash drums	Case 1: Rectisol process; temperature = -30 °C, P =1 bar Case 3: Rectisol process; temperature = 0 °C, P = 25 bar Remaining H ₂ S = 10 ppm
Methanol Synthesis	PFR reactor with separation facilities	PFR reactor working at 25 bar and 270 °C Graaf.et al Kinetics; Catalyst: Copper Zinc Alumina CZA
Water Gas Shift (WGS)	REquil (Reactor)	Two Equil reactors Molar H ₂ O/CO = 2; Catalyst: γ -Al ₂ O ₃ - α -Ga ₂ O ₃
CO ₂ Removal (AGR)	RadFrac and flash drums	Case 1 & 2: Rectisol process; temperature = - 30 °C, P = 1 bar Case 3: Rectisol process; temperature = 0 °C, P = 1 bar CO ₂ Removal = 99%

3.1.2 Governing Equations for the Technical Analysis

To evaluate our model, we calculated some crucial parameters from the literature that represent the design efficiency in terms of product quality, energy utilization, and cost reduction. **Table 8** shows some of the formulas used to evaluate our designs. HPF is the mass flow rate of produced hydrogen per total feedstock. The hydrogen and methanol

thermal energy were calculated from their lower heating value and their mass flowrates. The process efficiency and the CO₂ specific emission formulas were evaluated according to (Usama, 2021) [95]. The total investment cost (TIC) demonstrates the capital cost and the methanol and hydrogen rate of production. To calculate the capital investment cost, we used historical related data modified by Chemical Engineering Plant Cost Index (CEPCI). The exponent x is between 0 and 1, and its value was selected to be 0.6. The total fuel cost in €/kg represents the production cost of the fuel (hydrogen and methanol) in the dual production system. The SN ratio (the stoichiometric number) gives indication about the hydrogen to CO₂ content in the mixture [96]. SN should be around 2, and as it is larger, the gas heating value is higher [97].

Table 8 Main parameters calculation based on literature

Energy Analysis Equations	No.	Economic Analysis Equations	No.
$LHV_{Syngas} \left(\frac{MJ}{Nm^3} \right) = 12.636 y_{CO} + 10.798 y_{H_2}$	1	$Cost_{new} = Cost_{old} \times \left(\frac{Capacity_{New}}{Capacity_{Old}} \right)^x \times \frac{CEPCI_{New}}{CEPCI_{Old}}$	9
$HPF = \frac{\text{Produced } H_2 \left(\frac{kg}{h} \right)}{\text{Total Feed} \left(\frac{kg}{h} \right)} \times 100\%$	2	<i>Total Fixed Manufacturing Cost</i> = <i>Maintenance + Labor</i> + <i>Administrative, support & overhead costs</i>	10
$H_2 \text{ Thermal Energy} = H_2 LHV \left(\frac{kJ}{kg} \right) \times \text{Produced } H_2 \left(\frac{kg}{h} \right)$	3	$N_{OL} = (6.29 + 0.23 N_{np})^{0.5}$ N_{OL} is the number of operators per shift and N_{np} is nonparticulate processing steps	11
$CH_3OH \text{ Thermal Energy}$ $= CH_3OH LHV \left(\frac{kJ}{kg} \right)$ $\times \text{Produced } CH_3OH \left(\frac{kg}{h} \right)$	4	$Labor \text{ Cost} = N_{OL} \times Labor \text{ Cost per Shift}$ $\times \text{Daily \# of Shifts}$	12
$Total \text{ Consumed Energy (kW)}$ $= Hot \text{ Utility (kW)} + Cold \text{ Utility (kW)}$	5	$Total \text{ Fuel Cost} \left[\frac{\text{€}}{kg} \right]$ $= \frac{Hydrogen \& \text{Methanol Life Cost (€)}}{Hydrogen \& \text{Methanol Life Production Flow Rate (kg)}}$	13
$CO_2 \text{ specific Emissions} = \frac{Uncaptured CO_2 \left(\frac{kmol}{h} \right)}{(H_2 + CH_3OH) Production \left(\frac{kmol}{h} \right)}$	6	$Methanol \text{ Cost} \left[\frac{\text{€}}{kg} \right]$ $= \frac{Total \text{ Fuel Life Cost (€)}}{Methanol Life Production Flow Rate (kg)}$	14
$Process \text{ Efficiency } (\eta_{net})$ $= \frac{H_2 \text{ Thermal Energy (kW)} + CH_3OH \text{ Thermal Energy (kW)}}{Feed \text{ Thermal Energy (kW)} + Energy \text{ Consumed (kW)}}$ $\times 100\%$	7	$TIC \text{ per ton of } H_2 = \frac{Total \text{ investment cost}}{Hydrogen \& \text{methanol generation}}$	15
$SN = \frac{y_{H_2} - y_{CO_2}}{y_{CO} + y_{CO_2}}$	8	$Methanol \text{ Yield} = \frac{methanol \text{ production rate} \left(\frac{kg}{h} \right)}{syngas \text{ inlet flow rate} \left(\frac{kmol}{h} \right)}$	

3.1.3 Reaction Kinetics for Methanol Synthesis

The methanol synthesis operational conditions and kinetics were based on Graaf et.al (1989) [98]. The catalyst is Cu/Zn/Al with a temperature and pressure ranges from 210 - 290 °C and 15-50 bars [99]. To accurately develop the model and optimize the results, we selected 290 °C and 25 bars as the operational parameters for the methanol synthesis PFR. The process consists of three main parts (i.e., reactions) which are hydrogenation of carbon monoxide, hydrogenation of carbon dioxide, and reverse gas shift. The reactions and the kinetics are provided in **Table 9**. The table was designed to meet the Aspen plus interphase. The reaction constants were also provided in **Table 10**, **Table 11**, and **Table 12**. The reaction equilibrium constants in **Table 12** were introduced and given by Graaf et.al (1986) [100]. K_{P2} is the multiplication of K_{P1} and K_{P3} , because the CO_2 hydrogenation reaction is the sum of CO hydrogenation reaction and RWGS reactions.

Table 9 The main reactions and the reaction rate expression

Step Definition	Reaction	Rate of Reaction
CO Hydrogenation	$\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}$	$r_1 = \frac{k_1 K_{\text{CO}} \left[f_{\text{CO}} f_{\text{H}_2}^{1.5} - \frac{f_{\text{CH}_3\text{OH}}}{f_{\text{H}_2}^{0.5} K_{P1}} \right]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) \left[f_{\text{H}_2}^{0.5} + \left(\frac{K_{\text{H}_2\text{O}}}{K_{\text{H}_2}^{0.5}} \right) f_{\text{H}_2\text{O}} \right]}$
CO_2 Hydrogenation	$\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	$r_2 = \frac{k_2 K_{\text{CO}_2} \left[f_{\text{CO}_2} f_{\text{H}_2}^{1.5} - \frac{f_{\text{CH}_3\text{OH}} f_{\text{H}_2\text{O}}}{f_{\text{H}_2}^{1.5} K_{P2}} \right]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) \left[f_{\text{H}_2}^{0.5} + \left(\frac{K_{\text{H}_2\text{O}}}{K_{\text{H}_2}^{0.5}} \right) f_{\text{H}_2\text{O}} \right]}$
Reverse Water Gas-Shift	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$	$r_3 = \frac{k_3 K_{\text{CO}_2} \left[f_{\text{CO}_2} f_{\text{H}_2} - \frac{f_{\text{H}_2\text{O}} f_{\text{CO}}}{K_{P3}} \right]}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) \left[f_{\text{H}_2}^{0.5} + \left(\frac{K_{\text{H}_2\text{O}}}{K_{\text{H}_2}^{0.5}} \right) f_{\text{H}_2\text{O}} \right]}$

Table 10 Reaction rate constants (Graaf et al 1989)

$k = A e^{\frac{B}{RT}}$	A	B
k_1	4.89×10^7	-113,000
k_2	1.09×10^5	-87,500
k_3	9.64×10^{11}	-152,900

Table 11 Adsorption equilibrium constants (Graaf et al 1989)

$K = A e^{\frac{B}{RT}}$	A	B
K_{CO}	2.16×10^{-5}	46,800
K_{CO_2}	7.05×10^{-7}	61,700
$\frac{K_{H_2O}}{K_{H_2}^{0.5}}$	6.37×10^{-9}	84,000

Table 12 Reaction equilibrium constants (Graaf et al 1986)

$K_p = 10^{\frac{A}{T}-B}$	A	B
K_{P1}	5,139	12.621
K_{P2}	3,066	10.592
K_{P3}	-2,073	-2.029

To input the kinetic data to the ASPEN plus simulator, it has to be in special strategy.

The reaction was selected to be LHHW (Langmuir-Hinshelwood-Hougen-Watson). The

ASPEN plus has three different sections which are kinetic factor, driving force and

adsorption. The process state was selected to be vapor with a packed bed catalyst. The

ASPEN methodology in inputting the kinetic constants is based on the following formula.

$$\ln(K) = A + \frac{B}{T} + C \ln(T) + D T$$

Therefore, the reaction rate constants, the adsorption equilibrium constants, and reaction equilibrium constants will be written the following form respectively.

$$\ln(k) = \ln(A) + \frac{B/R}{T}$$

$$\ln(K) = \ln(A) + \frac{B/R}{T}$$

$$\ln(K_p) = \frac{B}{\log_{10}(e)} - \frac{A}{\log_{10}(e) T}$$

$$K_{P2} = K_{P1} \times K_{P3}$$

The kinetic factor (k) k is just A , and $E = -B$. The other constants were evaluated based on the above equations, and they were summarized in the appendix 2.

3.2 Development and Validation of Plastics to Hydrogen Process

3.2.1 Sole Hydrogen Production (Case 1-Base Case)

The hydrogen was successfully produced from plastics wastes (i.e., PE and PP) in five main steps. The first step is to decompose the solid plastics using a decomposer at high temperature (i.e., 650°C). Then, on the gasifier at higher temperature (900°C), syngas and other gases will be produced with hydrogen to CO molar ratio of 1.86. To maximize the hydrogen production, the gaseous mixture was introduced to water gas shift, however, the usual temperature in WGS unit is on the range of 190-300 °C [101]. Therefore, the mixture was cooled to 220 °C on syngas quench step. The output mixture from WGS has low quantity and higher amount of CO₂ (i.e., H₂/CO₂ of 2.86) with some traces of H₂S, thus, we needed to wash the hydrogen from carbon dioxide and H₂S in acid gas removal unit. We used methanol as an absorption agent in two stages. The first will be responsible to remove

hydrogen sulfide, and the second stage will purify the mixture from CO₂. The carbon dioxide and other gases are then separated from hydrogen using several stages of distillation columns and flash drums; where, the methanol was recycled at the needed cryogenic conditions (-37°C). **Figure 5** reveals the process base flow diagram.

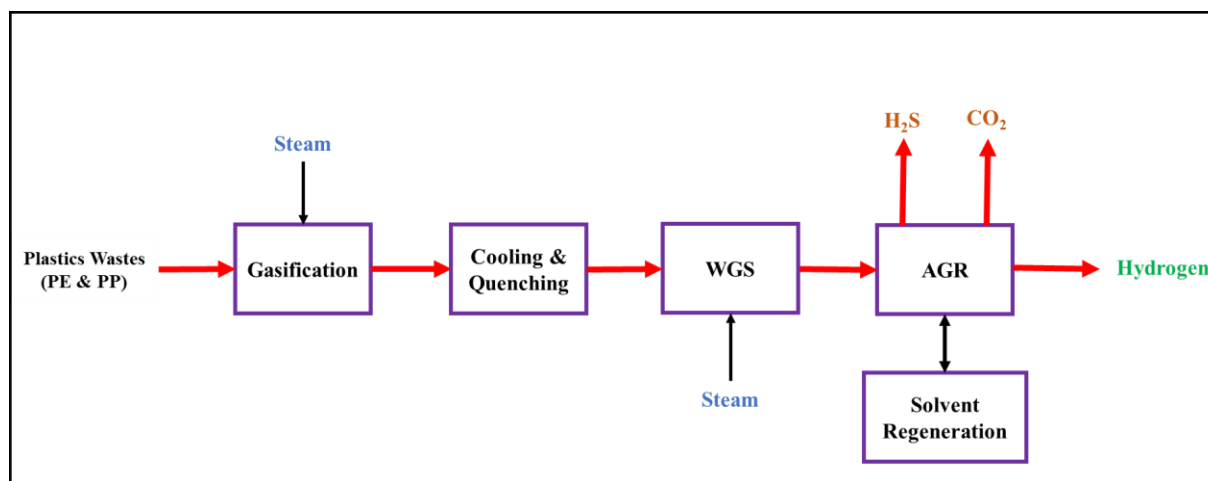


Figure 5 Producing hydrogen and methanol from waste plastics via conventional method (i.e., case 1)

To properly validate our gasification model, we start with proper building of the process, performing a critical review of several studies in the literature. Kannan et al. (2012, 2013, 2017) [102]–[107] studied the simulation of plastics (PE, LDPE, and PET) to syngas. They investigated the co-gasification of blend of PE and PET to syngas with energy recovery. Additionally, they studied the use of CO₂ as a gasifier agent instead of steam. However, all their publications were not properly validated such that I can trust their results. Their validation was based on having a similar trend with the published experimental paper [108], then the more updated publications were validated based on the previous one which is a combined validation error. Therefore, I did not consider their publications as a starting point since we do not have trustful reference. Surprisingly, Fanny and Henrik (2020) [109], conducted their results based on Kannan et al. previous studies, therefore, I also neglected

using their work as a reference. Dang et al. (2019) [91], studied the conversion of a blend of PP and PE to syngas. Fortunately, they validated some of their results from an experimental study for PP [110], then they confirmed their model to be used for PE and blend of PE with PP. The paper was clear and scientific, hence, I decided to take as a model for my study. Additionally, the feed stock compositions were taken from previous studies [111], [112] simulating gasification process through ASPEN PLUS. Their optimal result (i.e., H_2/CO of 2.1) was at $900^{\circ}C$, and steam to fuel ratio of 1.5 using RGibbs reactor for the gasification process. They also investigated the effect of steam to plastic feed ratio and the effect of PE to PP ratio on the LHV of syngas and H_2/CO .

Based on the mentioned study, we developed our study simulating the gasification process. To validate our results, we looked for experimental data when steam gasification is processed for PP and PE respectively [110] [113]. **Table 13** and **Table 14** show the comparison between the referenced deduced results and our base case results. We can perceive that, our results from steam gasification unit are highly matching with the experimental results from two different sources. Therefore, we built on this model for further investigation and study for hydrogen production.

Table 13 PP model validation for the gasification process at 800 °C and a mass ratio S/F of 2

PP			
Component	Reference Case (%)	Base Case (%)	Difference
H ₂	68.3	66.4	1.9
CO	26.1	27.5	-1.4
CO ₂	3.9	5.7	-1.8
CH ₄	1.3	0.3	1.0
Others	0.3	0.1	0.2

Table 14 PE model validation for the gasification process at 900 °C at a molar ratio of 2 (i.e., mass ratio of 188 to 100)

PE			
Component	Reference Case (%)	Base Case (%)	Difference
H ₂	68.6	67.4	1.2
CO	25.5	28.8	-3.3
CO ₂	1.1	3.7	-2.6
CH ₄	3.6	0.0	3.6
Others	1.2	0.0	1.2

3.2.2 Sole Hydrogen Production (Case 2-Alternative Case)

The reforming model (Case 2) is the integration of steam methane reforming (SMR) with plastic gasification to enhance the syngas heating value, and ultimately to exchange the gasification heat with SMR feed stream. The process base flow diagram is provided in **Figure 6**. We performed the integration of the two processes such that, we did not need external heat for SMR by controlling the natural gas feed rate. The scheme and design of the process was taken from Hamid et.al (2020) [93]. The process performed at atmospheric pressure which had been proved by several studies [114]–[116]. The natural gas consisting mainly of methane was mixed with steam to perform the process. The steam to methane molar ratio was set to be 1.50 and the inlet temperature was selected to be 895°C. Then, via RStoic and RGibbs reactors, the SMR process was performed with operational temperature of 894 and 900 °C respectively. The process reactions are provided in **Table 6**.

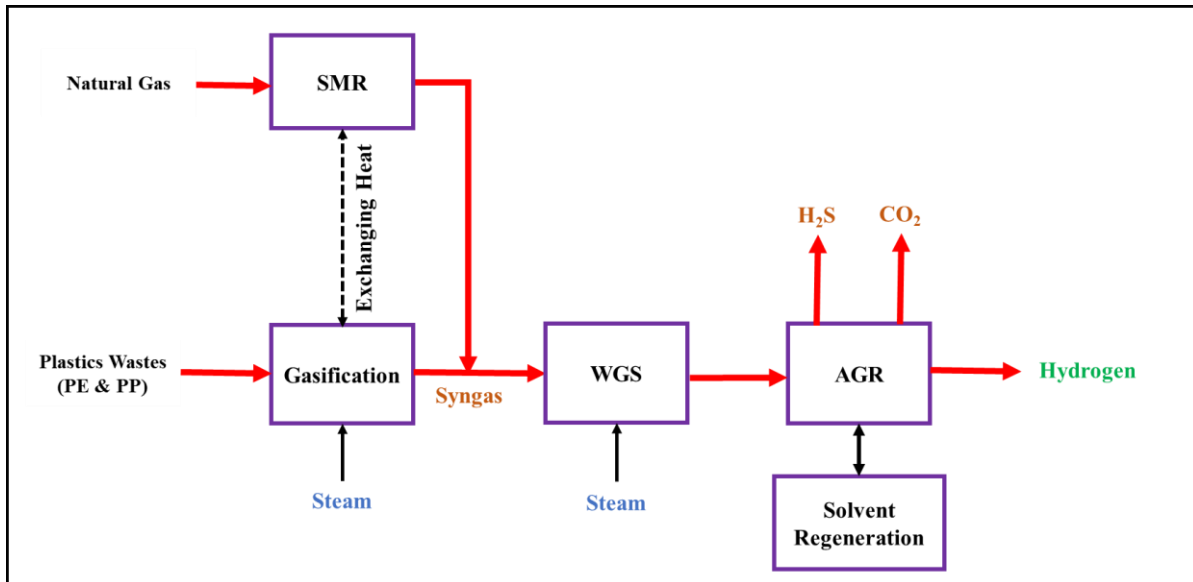


Figure 6 Producing hydrogen and methanol from waste plastics via integrated model with SMR process (i.e., case 2)

The SMR results were in good agreement with the literature in terms of hydrogen to carbon monoxide ratio. It had been found that, the hydrogen to carbon monoxide ratio was around 3.0, which was provided by Salwa et.al (2016) [117]. The syngas mixture coming from SMR, and gasification were mixed and introduced to WGS with the same conditions applied in base case design. The WGS operational conditions were confirmed from several studies [118], [119]. Additionally, the acid gas removal unit was designed based on those studies (i.e., Usama.et.al (2015) [120]; Umer et.al (2017) [121] ; Usama et.al (2015) [122]).

3.3 Development and Validation of Case Studies for Dual Hydrogen and Methanol Production

In the previous section, the main aim was to produce hydrogen from waste plastics (i.e., case 1 and case 2). This section focuses on methanol production from waste plastics, and the remaining hydrogen will be further processed to increase its purity. Therefore, it is a dual fuel production process producing hydrogen fuel and methanol simultaneously. As

case 2, the plastic gasification will be integrated with steam methane reforming to enhance the hydrogen purity and the overall process efficiency.

3.3.1 Dual Methanol and Hydrogen Production (Case 3-Base Case)

The hydrogen and methanol were successfully produced from plastics wastes (i.e., PE and PP) in five main processes. The first process is the decomposing of the solid plastics at high temperature (i.e., 650°C). Then, on the gasifier at higher temperature (1500°C) [123] and moderate pressure 25 bars, syngas and other gases were produced with H_2/CO molar ratio of 1.87. The outlet gas mixture was introduced to H_2S removal unit after cooling using lean as an absorber. The operational conditions of the absorber were 50°C, and 25 bars. The amount of H_2S was reduced to 1 ppm. The inlet temperature and pressure to methanol synthesis reactor were specified to be 290 °C and 25 bars meeting the experimental methanol synthesis operational conditions [124]. The methanol catalyst characteristics and the inlet specifications were based on Portha et al. (2017) [125] who extensively studied the Graaf.et. al kinetics to synthesize methanol. Although, the methanol reactions are exothermic, however, increasing the temperature enhanced the kinetic constants which was superior to the reduction in the equilibrium constants. Additionally, the process was performed at relatively moderate pressure based on sensitivity analysis performed on the gasifier conditions and the methanol and hydrogen production. The uncovered gases in methanol synthesis process were fed to WGS unit maximizing the hydrogen production, then via CO_2 removal unit, we produce relatively pure hydrogen. The WGS temperature was on the range of 190-300 °C [101] The WGS operational conditions were specified based on previous studies [118], [119]. Additionally, we designed the acid gas removal

units according to some previous studies (i.e., Usama et al. (2015) [120]; Umer et al. (2017) [121] ; Usama et al. (2015) [122]). **Figure 7** represents the process base flow diagram.

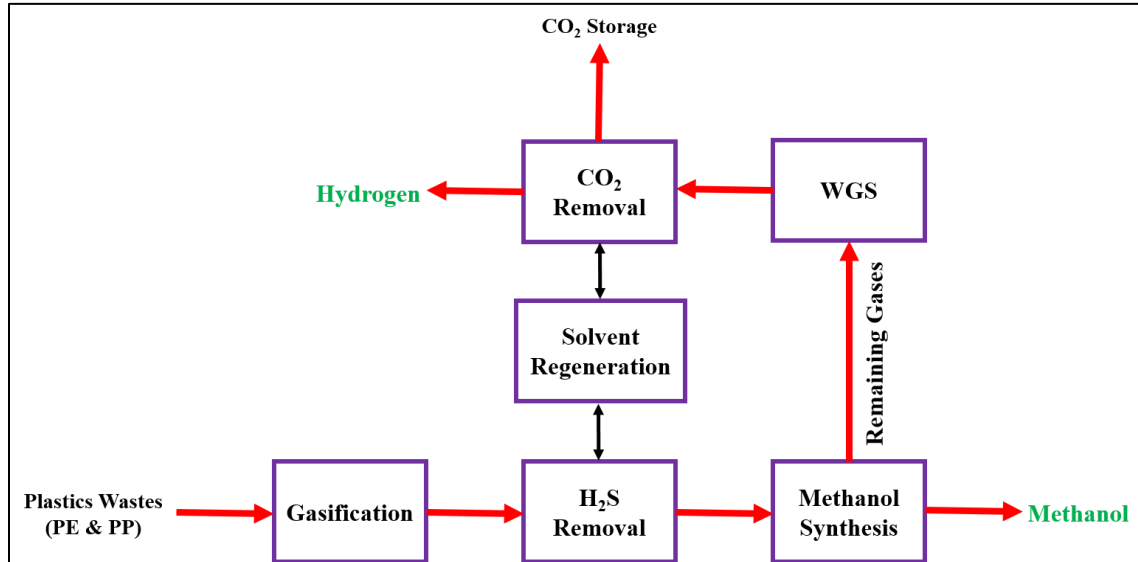


Figure 7 Producing hydrogen and methanol from waste plastics via conventional method (i.e., case 3)

We validated our model and the results for the syngas composition and methanol production from previous studies. Dang et al. (2019) [91], studied the conversion of PP and PE to synthesis gas. The successfully produced synthetic gas from the plastic blend (i.e., PE and PP) using ASPEN plus software. Their feed stock specifications were deduced two different studies [111], [112] . At a gasification temperature of 900°C and steam to plastic ratio of 1.5, optimal ratio of H₂/CO was achieved. Hence, we validated our results based on this study, and then we investigated the process further via sensitivity analysis. Due to design constrains, we increased the gasifier temperature and pressure to 1500 °C and 25 bars. We successfully produced synthetic gas with high SN and H₂/CO ratios. Additional validation for the gasification results using previous experimental studies on polyethylene and polypropylene [110] [113]. **Table 13** and **Table 14** demonstrate the gasification syngas composition for pure PE and pure PP. The results are highly matching with the

experimental one. Hence, our model was further developed toward hydrogen and methanol production. The methanol synthesis results were in the range of the results recorded by graaf.et.al (1990)[98].

3.3.2 Dual Methanol and Hydrogen Production (Case 4-Alternative Case)

The alternative model (Case 4) is basically, the incorporation of SMR and plastic gasification to boost the syngas heating value and exchange the heat of the outlet gasification stream with the SMR feed stream. The process base flow diagram is given in **Figure 8**. We controlled the SMR feed flow rate such that, the exchanged heat will be sufficient. The process scheme for SMR was taken from Hamid et al. (2020) [93]. The steam was mixed with the natural gas containing mainly methane. The steam to methane mass ratio was set to be 1.60 and the SMR inlet temperature and pressure were 895°C, and 1 bar. After that, RStoic and RGibbs reactors were modeled at temperature 894 and 900 °C respectively. The RStoic reactor was simulated at atmospheric pressure, where the RGibbs reactor pressure was 25 bars. Those operational conditions are in match with the literature [126], and they were selected for the design requirement maximizing the SN ratio with proper preparation for the methanol production process. The SMR reactions are provided in **Table 6**.

The hydrogen to carbon monoxide produced from SMR was in good agreement with the literature. Salwa et al. (2016) reported an optimal H_2/CO of 3.0 from the experimental studies, which was achieved in our model [117]. The gaseous mixture from gasification and SMR were mixed and introduced to H_2S removal unit to remove the H_2S traces that might block the methanol catalyst [127]. Then, the cleaned gas was fed to the methanol synthesis process with the appropriate conditions. The methanol was successfully

produced, and the unconverted gases were mainly hydrogen (94% molar purity) with traces of methane. Since the CO and CO₂ were converted completely with the aid of the recycling stream, we did not need further gas processing. Hence, methanol and hydrogen were simultaneously produced. This result was achieved by performing extensive sensitivity analysis to control the feed specifications enhancing the SN ratio to 2.51.

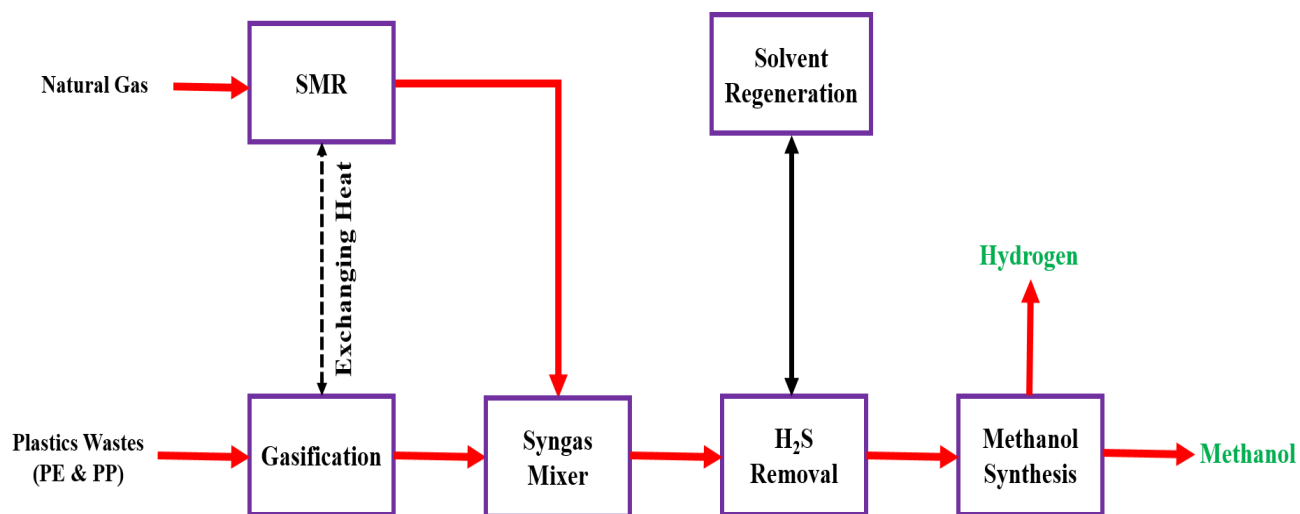


Figure 8 Producing hydrogen and methanol from waste plastics via integrated model with SMR process (i.e., case 4)

An additional validation analysis was performed comparing the two designed cases for methanol production and two previous studies with similar operational conditions[99], [128]. The key parameter in the comparison was the methanol yield which was defined as the mass production rate of methanol per syngas molar flow rate. The comparison is provided in **Figure 9**.

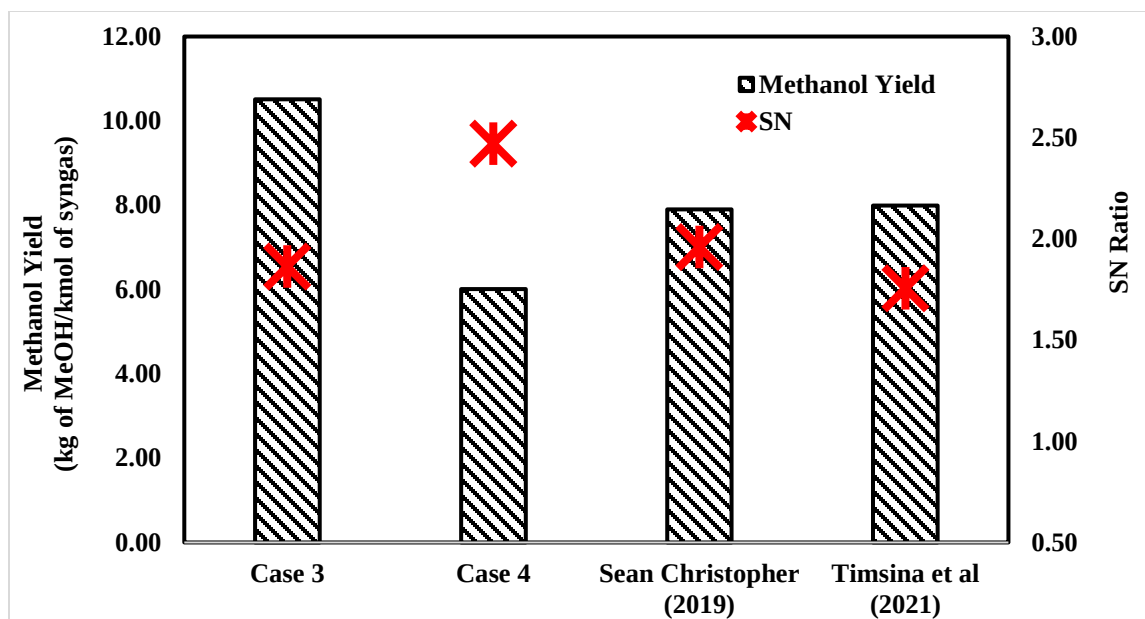


Figure 9 Validation of case 3 and case 4 in terms of methanol yield

CHAPTER 4

RESULTS AND CONCLUSION

Two different models were designed to produce hydrogen and methanol after simulating the whole units (Gasification, SMR, WGS, and AGR). To compare the two models (the base case and reformer case), we performed energy and economic analysis. Additionally, those results were matched with the literature. Furthermore, carbon dioxide emissions were also calculated because we are targeting reduction of those emissions. The main parameter representing the energy analysis is the process efficiency. The hydrogen life cost was the parameter demonstrating the economic analysis. The reforming model was better than base case models in terms of energy efficiency, hydrogen production cost, and carbon dioxide emissions.

4.1 Process Performance Analysis and Fuel Production Rates

4.1.1 Hydrogen Production Model (Case 1 and Case 2)

The plastic flowrate was chosen considering the steam flowrate such that, the steam to plastic ratio will be maintained 1.25. In the gasification process, more carbon monoxide was produced with less amount of hydrogen. Comparing to the base case, the molar ratio of H_2 to CO before the water gas shift was higher in case 2 than case 1 by 20 %, where the H_2 to carbon dioxide ratio was less by 62%, which proves the enhancement in the syngas heating value when alternative design was used. On the other hand, the H_2 to CO after WGS was less in case 2 when compared with case 1 by 80 %. The carbon dioxide emission after WGS was lower in case 2 by 11%. Hence, the alternative design is more convenient and efficient than the base case in terms of product quality and carbon dioxide emissions. The hydrogen sulfide after WGS was also lower for case 2 by 19%. **Table 15** represents the operational conditions for the most essential units.

Table 15 Outlet flowrates of each process at each unit and stream composition

	Plastics	Steam (Gasifier)	Gasifier (RGibbs)	Reformer	Syngas Mixer		WGS Unit		AGR Unit (H ₂ Storage)		CO ₂ Storage	
	Case 1 & 2	Case 1 & 2	Case 1 & 2	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
T (°C)	300	300	900	220	220	221	10	10	25	25	25	25
P (bar)	1.013	1.013	1.013	1	1	1	1	1	1	1	1	1
Mass Flow (kg/h)	100	125	225	109	224.58	333.58	469.38	578.38	49.58	75.22	226.40	337.53
Mole (%)												
H ₂		-	0.636	0.683	0.636	0.653	0.579	0.654	0.976	0.978	0.0026	0.0026
CO		-	0.341	0.206	0.341	0.292	0.001	0.004	0.002	0.006	2.5E-05	6.8E-05
CO ₂		-	0.002	0.020	0.002	0.008	0.202	0.206	0.003	0.003	0.993	0.994
H ₂ O		1	0.004	0.089	0.004	0.034	0.206	0.128	0	0	0	
CH ₄		-	0.017	0.001	0.017	0.011	0.010	0.008	0.016	0.011	0.0018	0.0012
N ₂		-	7.5E-04	1.8E-03	7.5E-04	1.1E-03	4.5E-04	7.9E-04	7.4E-04	1.2E-03	3.4E-05	5.4E-05
H ₂ S		-	1.8E-04	-	1.8E-04	1.1E-04	1.1E-04	8.0E-05	~0	~0	1.2E-07	1.2E-07
CH ₃ OH		-	0.00	-	-	-	-	-	1.8E-03	1.8E-03	0.0023	0.0023
Molar H ₂ /CO	-	-	-	3.32	1.86	2.23	-	-	-	-	-	-
Molar H ₂ /CO ₂	-	-	-	33.34	389.50	77.43	2.86	3.18	-	-	-	-

We investigated the overall efficiency of the two cases by considering several, essential parameters (i.e., **Table 16**). The first parameter is the hydrogen purity after the acid gas removal unit, which was proven to be greater in the second case by 0.15% when compared to the first case. The overall efficiency of the process in terms of feedstock conversion was calculated and represented by HPF which found to be greater in case 2 by 5.6%. Additionally, we evaluated the two cases in terms of heating value (i.e., lower, and higher). We concluded that, the second case has lower and higher heating value than the first one by 5.7%, and 5.0% respectively. To deeply investigate the two cases, we performed the energy analysis which finally was represented by process efficiency which found to be greater in case 2 than case 1 by 6.43 % when compared to the first case. Therefore, the alternative case seems to be more efficient than the base case, however, we needed to also study the economic part to fully understand the picture.

Table 16 Comparison between the two designed models in terms of energy calculation

Characteristic/Model Type	Case 1	Case 2
Produced hydrogen per total feed (mass %)	50	52.8
Hydrogen purity (mol %)	97.62	97.77
Syngas gross heating value GHV (MJ/kg)	26.18	27.67
Syngas net heating value LHV (MJ/kg)	23.55	24.73
Feed Stock Energy (kWth)	1198.61	1757.07
Thermal Energy of Produced H ₂ (kWth)	1385.25	2060.59
Min Hot Utilities Required (kW)	757.06	1069.75
Min Cold Utilities Required (kW)	200.80	187.06
Total required energy after heat integration (kW)	957.86	1256.81
Process Efficiency(η_{net}) (%)	64.24	68.37

4.1.2 Dual Hydrogen and Methanol Production Model (Case 3 and Case 4)

Table 17 provides the operational conditions for the main units for case 3 and case 4. The steam to plastic ratio was 1.25 and it was confirmed in our previous study producing sole hydrogen. The temperature was 300 °C with atmospheric pressure. Then, the steam and plastics will be mixed on the gasifier which operates at high temperature and pressure. The outlet composition from the gasifier had a H₂/CO ratio of 1.87 with SN of 1.86. The CO₂ production was extremely lower than the carbon monoxide. The SMR operates at 25 bars and produces 389 kg/h of syngas which is 63.4% of the total produced syngas. It produces higher H₂/CO and SN ratios when compared to the plastic gasification by 69.9% and 57.6% respectively. Then the two syngas streams were mixed for case 4 which resulted in enhancement of the syngas heating value. After that, the synthesis gas was cleaned from H₂S via H₂S removal unit. The composition was slightly changed because only H₂S was removed with traces of CO₂. In methanol synthesis unit, we successfully produced the methanol with very high purity in both cases. Case 4 had higher methanol purity than case 3 by 0.83%. The case 4 directly produces hydrogen, therefore, the WGS and CO₂ removal units were not required. The outlet hydrogen content in the unconverted gas from methanol synthesis unit was negligible, however, the WGS unit increases the hydrogen mole composition to 39% with a CO₂ content of 39% as well. Therefore, AGR unit was required to remove the carbon dioxide. The produced hydrogen in case 3 was at the outlet of CO₂ removal unit with a rate of 6.15 kg/h. The purity of hydrogen was low because of the remaining methane from the plastic gasification unit. The alternative case produces higher hydrogen rate than case 3 with a superior purity than the base case by 49%. Therefore, the results clearly stated a superior performance of case 4 than case 3.

Table 17 Mainstream specifications and the unit outlet results

	Plastics	Steam (Gasifier)	Gasifier (RGibbs)	SMR	Syngas Mixer	H ₂ S Removal	Methanol Unit	WGS Unit	CO ₂ Removal	CO ₂ Storage	H ₂ Product
	Case 3 & 4	Case 3 & 4	Case 3 & 4	Case 4	Case 3	Case 4	Case 3	Case 4	Case 3	Case 3	Case 4
T (°C)	300	300	1500	667	50	50	50	24	10	25	24
P (bar)	1.013	1.013	25	25	25	25	1	1	1	1	1
Mass Flow (kg/h)	100	125	225	389.286	224.58	613.862	229.175	578.566	213.32	545.702	23.6833
Mole (%)											
H₂	-	64.140	67.174	64.140	66.160	63.699	69.367	0.000	0.002	39.236	63.439
CO	-	34.377	21.182	34.377	25.591	34.039	26.725	0.223	0	0.016	0.025
CO₂	-	0.019	1.252	0.019	0.840	0.014	0.669	0.029	0	39.328	6.355
H₂O	1.0	0.127	9.949	0.127	6.668	0.000	0.000	0.000	0	0.960	0.000
CH₄	-	1.245	0.259	1.245	0.588	1.208	0.599	0.579	0.020	18.867	28.052
N₂	-	7.45E-02	0.183	7.45E-02	1.47E-01	0.073	1.52E-01	1.80E-02	1.25E-03	1.248	1.95E+00
H₂S	-	1.78E-02	-	1.78E-02	5.95E-03	0.000	1.00E-04	2.75E-04	2.19E-04	1.70E-04	0.178
CH₃OH	-	-	-	-	0.006	0.966	2.488	99.151	99.976	0.345	1.80E-03
Molar H₂/CO	-	1.866	3.171	1.866	2.585	1.871	2.596	-	-	0.998	-
Molar H₂/CO₂	-	-	53.645	-	78.759	-	-	-	-	-	-
SN Ratio	-	1.864	2.938	1.864	2.471	1.870	2.508	-	-	-	-

Table 18 shows the essential evaluated parameters which represent the performance of the base case and the alternative one. The results revealed a dominance of case 4 performance over case 3. The heating value of the total syngas represented by H₂/CO and SN ratios, for case 4 is greater than case 3 by 2.65 MJ/kg. The normalized production rate of hydrogen per total feedstock in case 4 is greater than case 3 by 4.04 (i.e., 66%) with a higher H₂ purity by 30%. The methanol production rate for the two cases were also evaluated, and the result revealed an enhancement in case 4 by 2.8%. The purity of the methanol is slightly larger in case 4. We achieved higher syngas conversion to methanol in the alternative case than the base case by 1.84%. A terminology that represents the energy performance is the process efficiency which was improved by 12.7% for case 4. Hence, the alternative case showed significant improve in the production rate and in the energy performance.

Table 18 The major evaluated parameters representing the energy analysis for the two cases

Characteristic/Model Type	Case 3	Case 4
Total syngas H ₂ /CO	1.87	2.60
Total syngas SN	1.87	2.51
Produced hydrogen per feedstock (mass %)	6.15	10.19
Produced hydrogen purity (mole %)	63.44	94.40
Produced methanol per feedstock (mass %)	2.12	2.18
Produced methanol purity (mole %)	99.94	99.98
Total syngas conversion to methanol (mass %)	92.48	94.32
Syngas gross heating value GHV (MJ/Kg)	26.10	29.39
Syngas net heating value LHV (MJ/Kg)	23.46	26.11
Feed Stock Energy (KW)	1198.61	3194.53
Thermal Energy of Produced H ₂ (KW)	70.64	616.66
Thermal Energy of Produced Methanol (KW)	1172.69	3019.63
Min Hot Utilities Required (KW)	538.46	1169.07
Min Cold Utilities Required (KW)	7.91	162.60
Total energy required after heat integration (KW)	546.37	1331.67
Process Efficiency (%)	71	80

4.2 Syngas Composition Analysis

4.2.1 Syngas Composition at WGS Outlet for Case 1 and Case 2

The hydrogen produced at the outlet of WGS was higher in case 2 than case 1 with higher molar composition (i.e., **Figure 10**). The main reason for that, is the more hydrogen rich syngas was achieved at the inlet of WGS. This indicates higher heating value for the alternative case than the base one. The amount of carbon monoxide is minimal in the two cases which implies the efficiency of WGS in converting carbon monoxide into hydrogen and carbon dioxide. There is an appreciable amount of carbon dioxide which will be removed along with hydrogen sulfide in AGR unit. The traces of methane in the two cases are similar in the two cases, however, it is slightly greater in the base case because of comparatively low gasification temperature in our process.

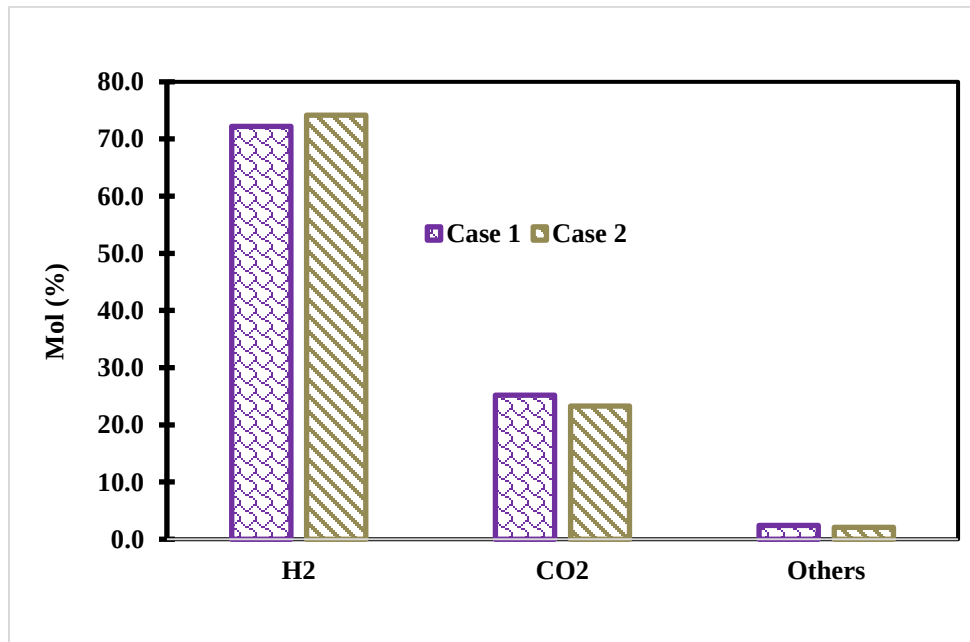


Figure 10 Comparison between base model and methane reforming model in terms of outlet syngas composition after WGS unit

Additionally, the hydrogen to carbon monoxide ratio at the inlet of WGS was evaluated for the base and alternative cases (i.e., **Figure 11**). It had been found that, the ratio was greater

for case 2 than case 1, indicating a higher heating value for the integrated process. The integrated process produced more hydrogen than the classical one because of the SMR unit that produced a hydrogen mole fraction of 67%. The overall energy process efficiency was calculated and studied, and it had been found that, it was higher in case 2 than case 1 by 6.43% when compared to the first case. By that, the case 2 is more efficient than case 1 in terms of heating value. However, economic analysis had to be performed to confirm the final preference of the alternative case.

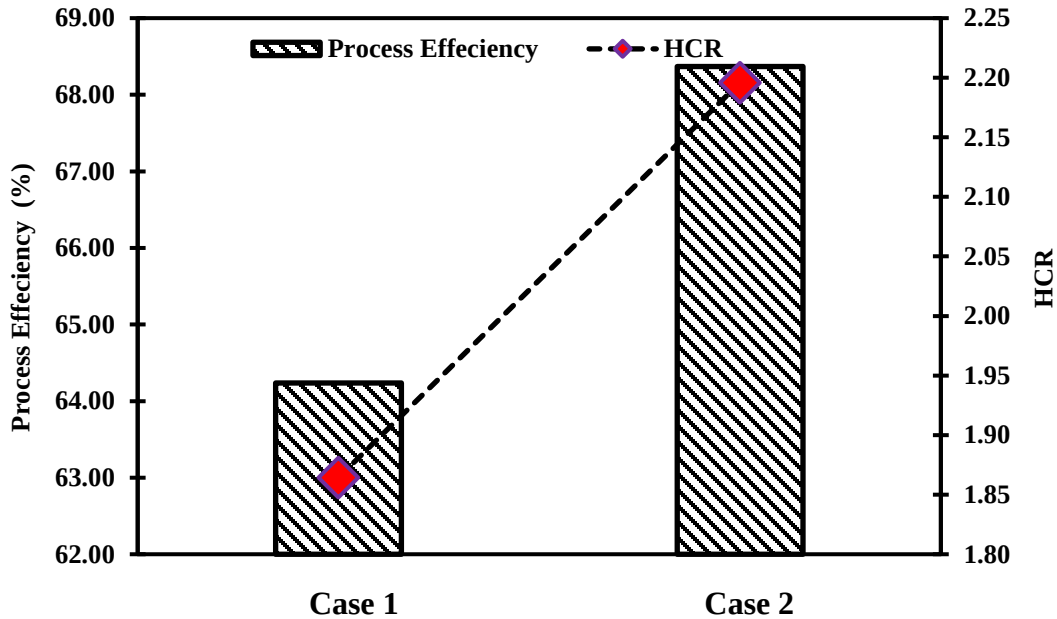


Figure 11 Comparison between base case and alternative case in terms of the total process efficiency and molar ratio of hydrogen to carbon monoxide before WGS

4.2.2 Composition of Syngas at the Inlet of Methanol Reactor for Case 3 and Case 4

A more illustration in the process performance is given in this section, which includes the synthesis gas composition at the inlet to methanol process, the process efficiency, and the normalized methanol production. **Figure 12** Comparison between base model and alternative model in terms of syngas composition at the inlet to methanol synthesis process shows the hydrogen and carbon monoxide contents in the synthesis gas prepared for

methanol synthesis. The gas compositions were suited for methanol synthesis; validated earlier with a hydrogen sulfide of 1 ppm. The carbon monoxide in case 3 is higher than case 4 by 21.5%. The alternative case produces more hydrogen since SMR process produces syngas with a higher H_2 . The content of hydrogen in case 4 is higher than case 3 by 8.9%. The two cases have high LHV, however, case 4 has higher hydrogen content. That preference in hydrogen content was not for methanol enhancement in the production rate, however, it was perceived in the final production rate of hydrogen fuel.

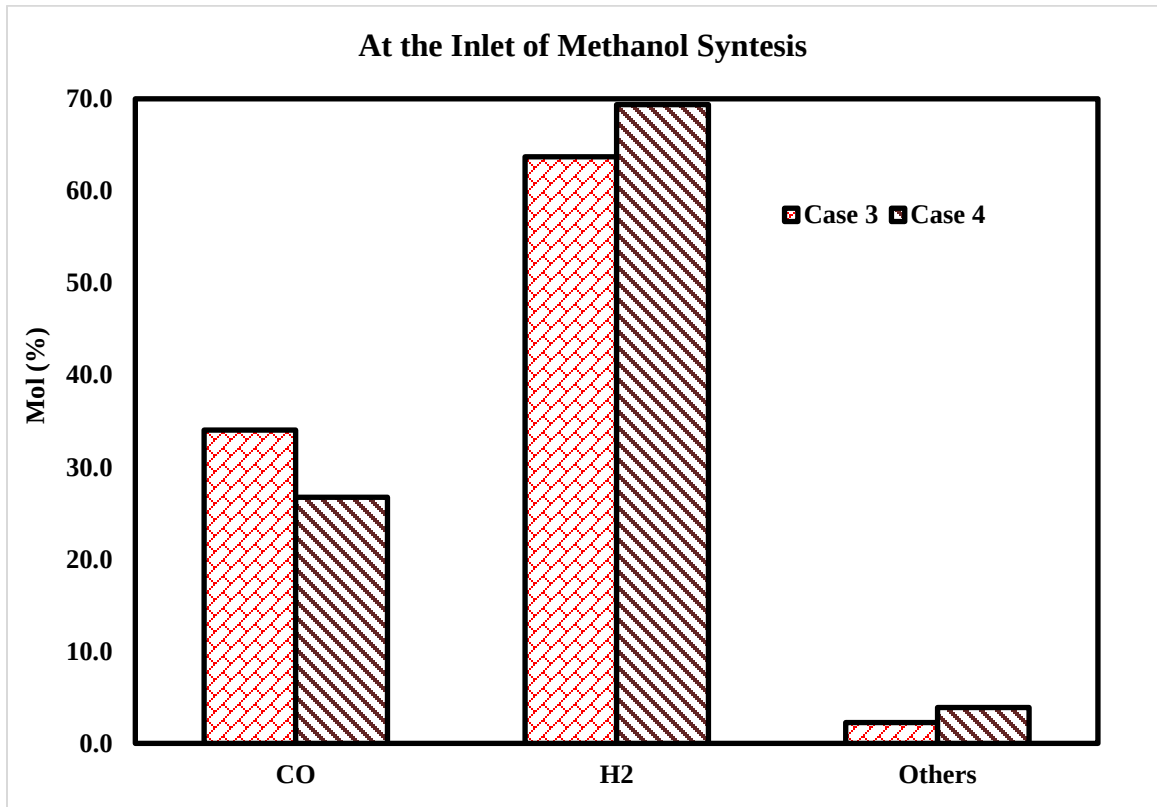


Figure 12 Comparison between base model and alternative model in terms of syngas composition at the inlet to methanol synthesis process

The alternative case had higher process efficiency than case 3 with 9% enhancement. This improvement is attributed to the energy integration between plastic gasification and SMR, which results in strong reduction in energy consumption. Additionally, with the alternative model, the production rate and fuel heating value had significantly increased. **Figure 12**

Comparison between base model and alternative model in terms of syngas composition at the inlet to methanol synthesis process demonstrates the overall process efficiency with the methanol final production rate for the two developed cases. The normalized methanol production rate was higher in case 4 than case 3 by 2.81%. The SN for the inlet syngas in case 4 was 2.51 which is the optimum for methanol synthesis [129]. In terms of fuel production, fuel heating value, and energy reduction, case 4 was superior to case 3. Therefore, with the new novel design case, we enhance the process of plastic thermal processing to be more feasible. The economic analysis is crucial to study the applicability of the two cases in the industry.

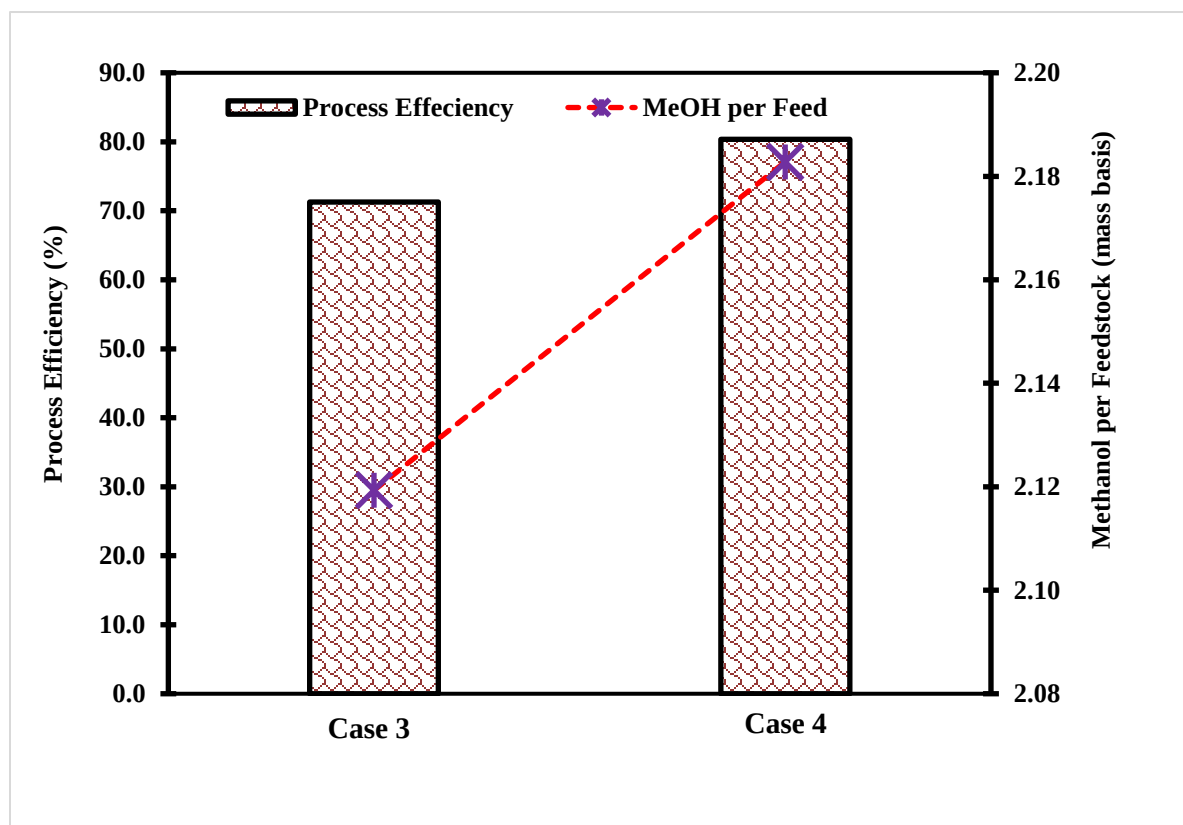


Figure 13 The process efficiency and normalized production rate of methanol for case 3 and case 4

4.3 CO₂ Specific Emissions

4.3.1 Analysis of CO₂ Emissions from Case 1 and Case 2

The carbon dioxide specific emissions were less in both cases; however, the alternative case has lower emissions by 1.2%. A study conducted by Usman et al. (2021), about the conversion of coal to hydrogen found that, the CO₂ specific emissions are in the level of 0.70 [93]. **Figure 14** shows the carbon dioxide specific emissions for each case along with HPE (Hydrogen per total feed; mass ratio). The HPF for case 2 is much stronger than case 3 with less carbon emissions. Hence, the alternative case was successful in producing higher amount of hydrogen from the normalized feedstock with a minimal emissions of carbon dioxide.

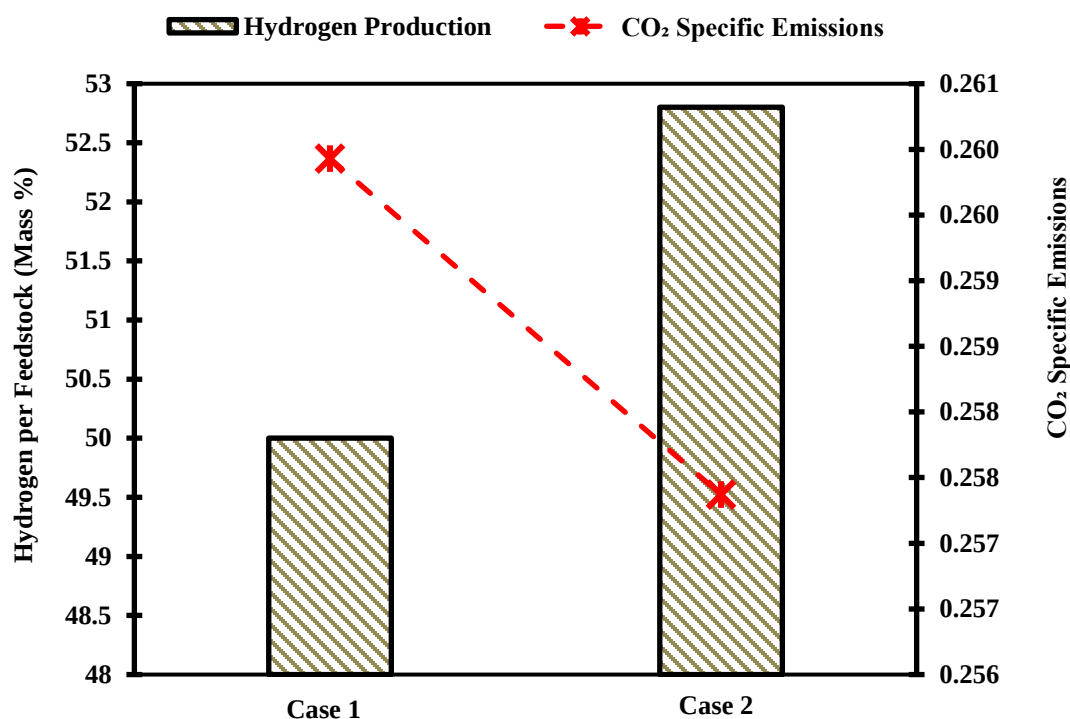


Figure 14 Comparison between base model and methane reforming model in terms of mass conversion of the feed to hydrogen and in terms of CO₂ specific emissions (CSE)

4.3.2 Analysis of CO₂ Emissions from Case 3 and Case 4

Controlling the CO₂ specific emissions for our study is very essential because we wanted to investigate a new energy source minimizing the waste pollution. Therefore, we performed extensive sensitivity analysis and developed acid gas removal unit to ensure lowest CO₂ emissions in the two modeled cases. We achieved a minimal CO₂ emission in the two cases, and surprisingly, our alternative case was very efficient in the reduction of carbon dioxide. Case 4 when compared to case 3 was higher by 0.0246. Hence, the carbon dioxide in case 4 is negligible. **Figure 14** shows the carbon dioxide specific emissions and the hydrogen production rate per total feedstock (i.e., plastics and natural gas). The normalized hydrogen production rate for the alternative case was higher by 66.7%.

Therefore, with the new alternative design, we highly limited the CO₂ specific emissions with significant enhancement in fuel production rate.

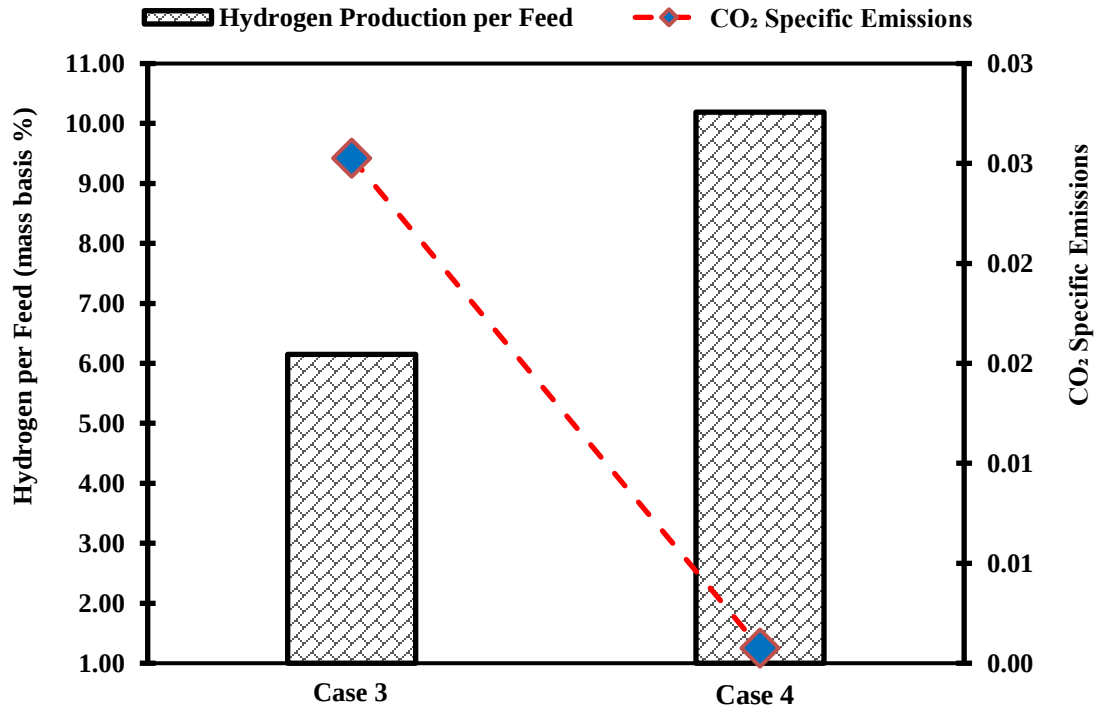


Figure 15 Comparison case 3 and case 4 in terms of CO₂ specific emissions (CSE) and normalized hydrogen production rate (HPF)

4.4 Sensitivity Analysis

4.4.1 Analysis of Case 1 and Case 2

After selection of the type of plastics, the simulation methodology, and guided reference, we validated our gasification results as in **Table 13** and **Table 14**. The results were matched and showed good agreement with the literature. Therefore, we continued modeling the other processes to produce hydrogen. We have done sensitivity analysis on gasification unit to properly select the optimal operational parameters (i.e., temperature, pressure, steam to feed ratio, and PE and PP blending ratio). We found that, the optimal conditions are when the blending mass ratio of PE/PP is 1 at atmospheric pressure on the gasifier, and

900 °C using steam to feed mass ratio of 1.25. Additionally, we studied the impact of some parameters on the performance of WGS unit (i.e., pressure, cooling rate, and steam flow rate). The optimal conditions deduced from this unit were at atmospheric pressure with a cooling rate of 30 KW, and steam to CO molar ratio of 1.0. The whole analysis is given in the following sections.

4.4.1.1 Sensitivity Analysis around Steam Gasification

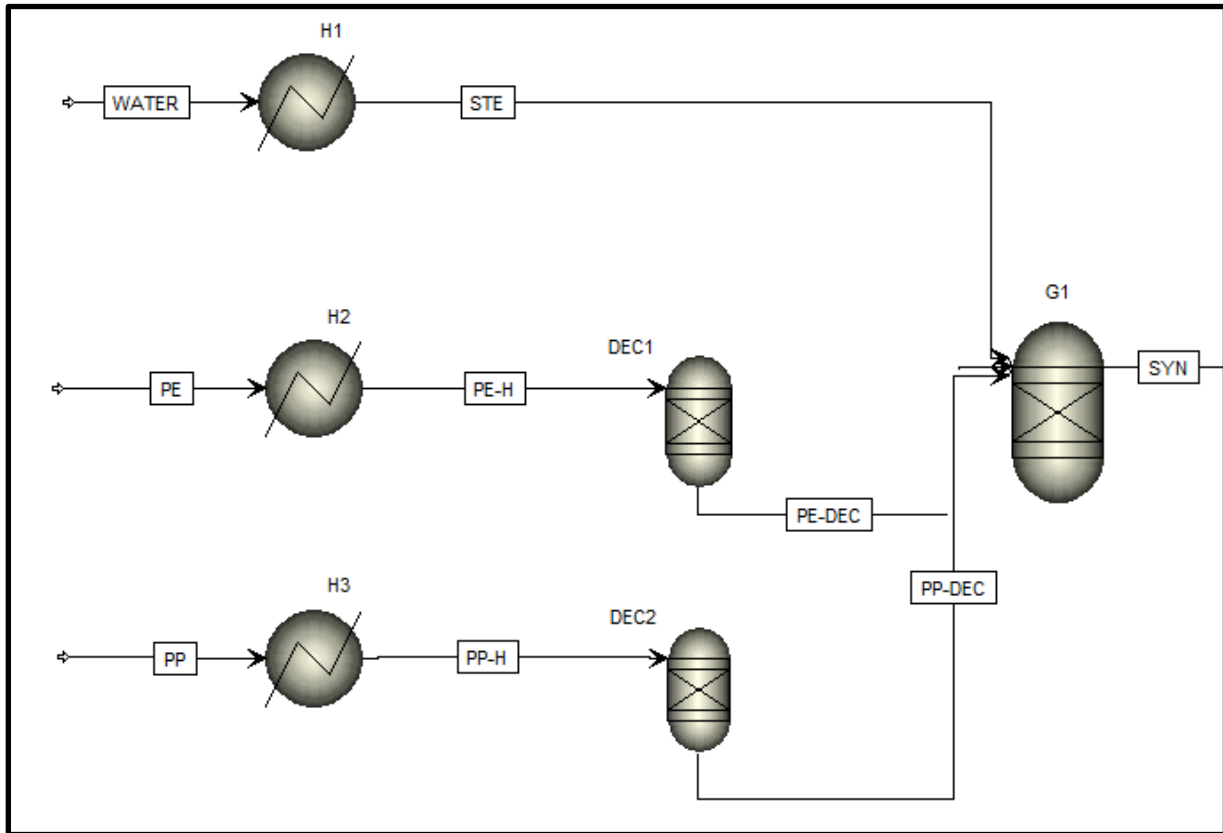


Figure 16 Scheme diagram for the plastic gasification process

The gasification process was started with heating the feedstock to 650 °C to meet the decomposer requirement. The feedstock (polyethylene and polypropylene) in parallel with specified amount of steam were fed to the decomposer to convert them to their elemental components. Then, they were gasified in G1 (RGibbs) at 950 °C converting the elemental components to syngas with some traces of hydrogen sulfide and carbon dioxide. Little

amount of steam was in the outlet, and they were separated after cooling the mixture.

Figure 16 illustrate the gasification process done via Aspen Plus software.

a. The Effect of Steam to Feed Ratio on Syngas Composition at the Outlet of the Gasifier

To calculate the low heating value of syngas (LHV), we used the following [91]. y_{CO} and y_{H_2} are the mole fraction of hydrogen and carbon monoxide respectively.

$$LHV_{syngas} = 12.636y_{CO} + 10.798 y_{H_2}$$

Figure 17 represents the sensitivity analysis on steam gasification unit investigating the impact of steam to plastic ratio (S/P or S/F) on syngas heating value. Although, increasing the steam to plastic ratio, decreased the CO production rate, however, it dramatically, enhanced the hydrogen production. CH₄ was suppressed when we increased the ratio of S/P. The optimal steam to feed ratio at 900 °C from the plots was 1.25, because further increase had a negligible impact on syngas LHV. The analysis was done at an equal blend of PE and PP. We concluded that, increasing the steam to plastic ratio has a positive impact on enhancing the syngas heating value, however, at a specific point, it will decrease again. Therefore, we considered the optimal ratio (S/P) which was 1.25.

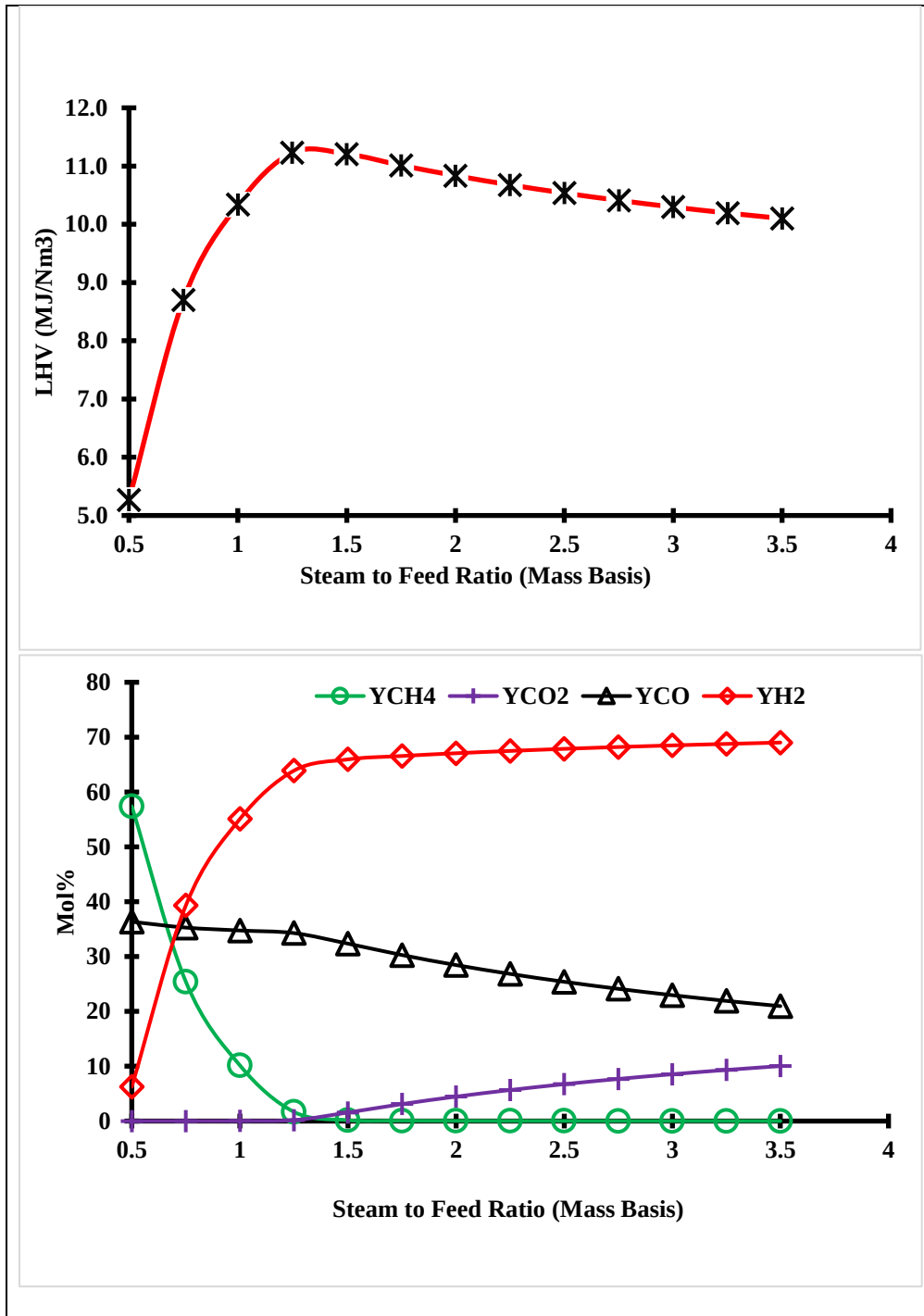


Figure 17 An equal blend of PE and PP steam to feed ratio effect on produced moles distribution and LHV at 900 °C

b. The Effect of Gasification Temperature on Syngas Composition

Lower gasification temperature promotes carbon dioxide due to the Boudouard reaction, which is basically, the reaction of CO_2 with carbon to produce CO . It is endothermic

reaction, thus, as the temperature increases, less carbon dioxide is produced [130]. Therefore, increasing the temperature has a positive effect on the heating value of the produce syngas. However, we found that, at a specific temperature, there was no further enhancement on the syngas heating value. We selected steam to feed ratio of 1.0, with PE/PP ratio of 1.0. A blend of PE and PP has a high LHV. **Figure 18** shows the impact of gasifier temperature on gasification process. Hence, gasification temperature of 900 °C was selected to be the optimal temperature for further investigation in this process.

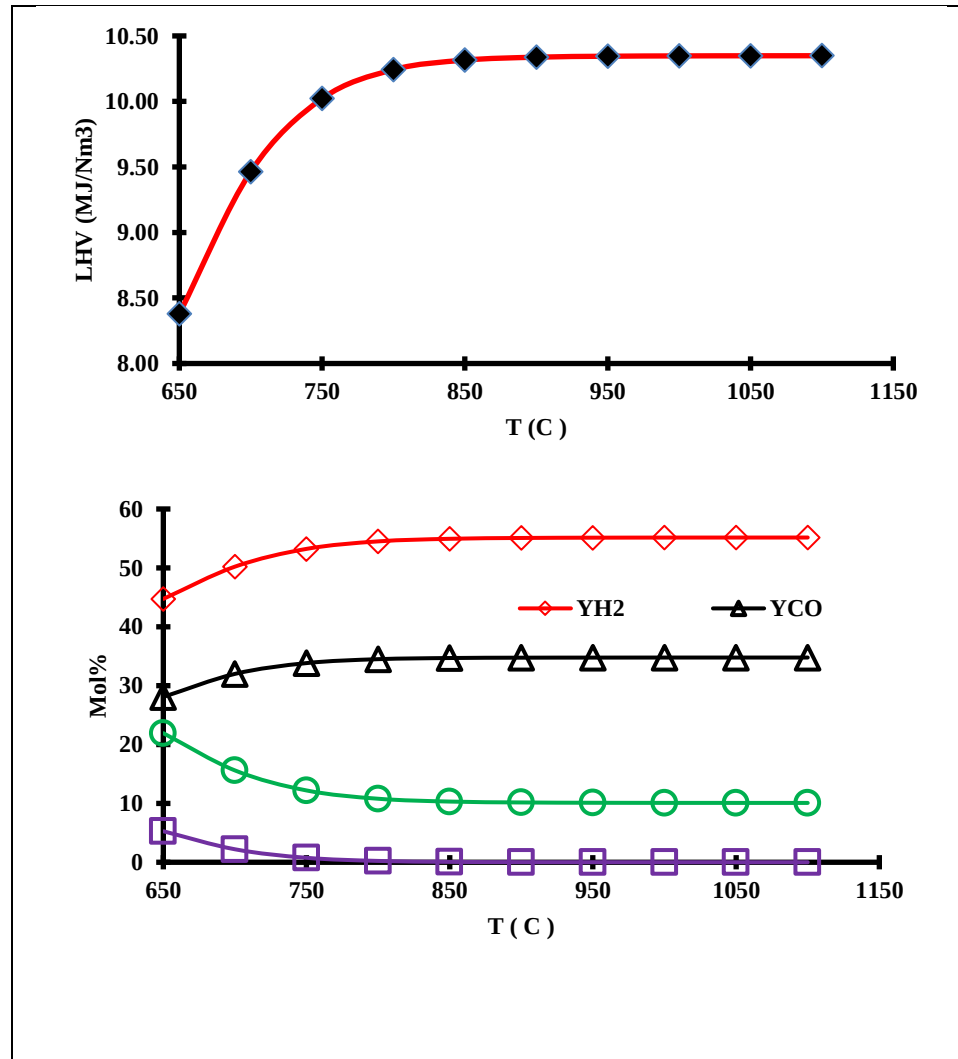


Figure 18 An equal blend of PE and PP gasification temperature effect on gases production distribution and LHV at mass ratio of S/P 1

c. Effect of PE to PP blend on Syngas Composition

We considered the plastic feed to be polyethylene (PE) and polypropylene (PP) due to their availability and satisfactorily heating value [131] [132]. The blend mass ratio of PE to PP had been studied with respect to temperature and steam to feed ratio. Four different mass ratios were investigated seeking the impact of the blend ratio on the overall heating value of the produced syngas.

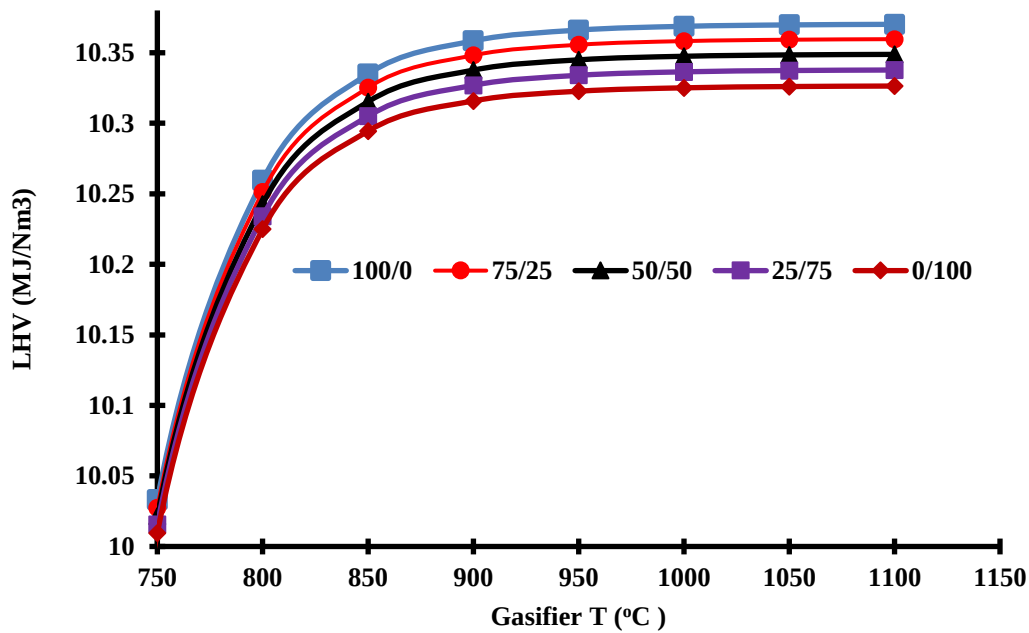


Figure 19 Effect of gasification temperature and plastic blend on syngas at steam to feed ratio of 1 (PE/PP mass basis)

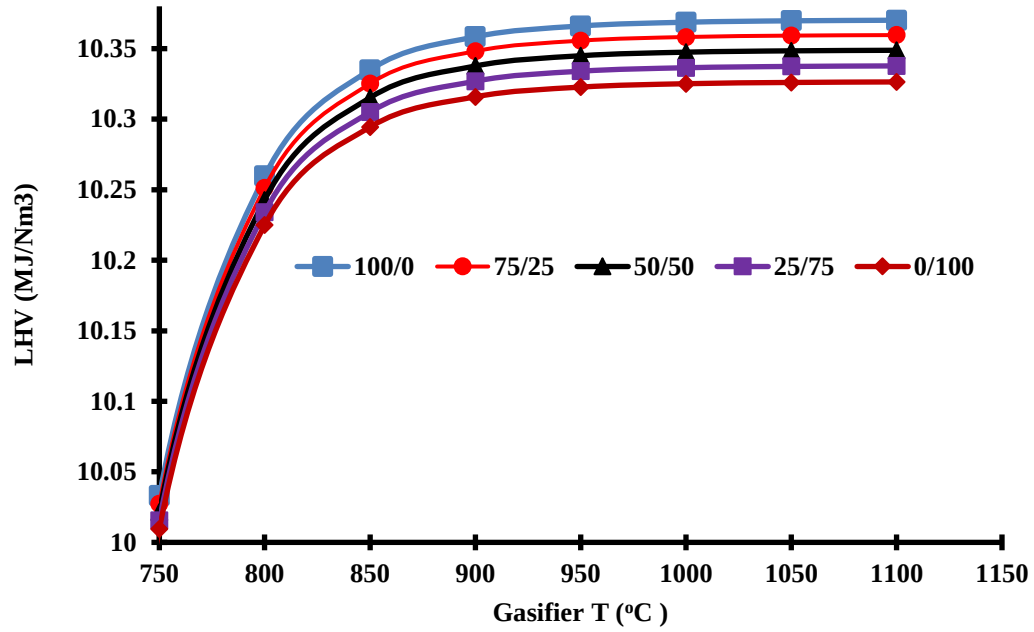


Figure 19 shows the syngas heating value versus the gasifier temperature for each blend ratio. The analysis was performed at steam to feed ratio of 1.0. The results indicated the superiority of having more polyethylene on the heating value. It is fundamentally because of higher heating value of polyethylene than polypropylene, which will impact the syngas heating value [133] [134]. Additionally, for the whole blending ratio, the optimal temperature was around 900°C, which was dedicated in the previous section.

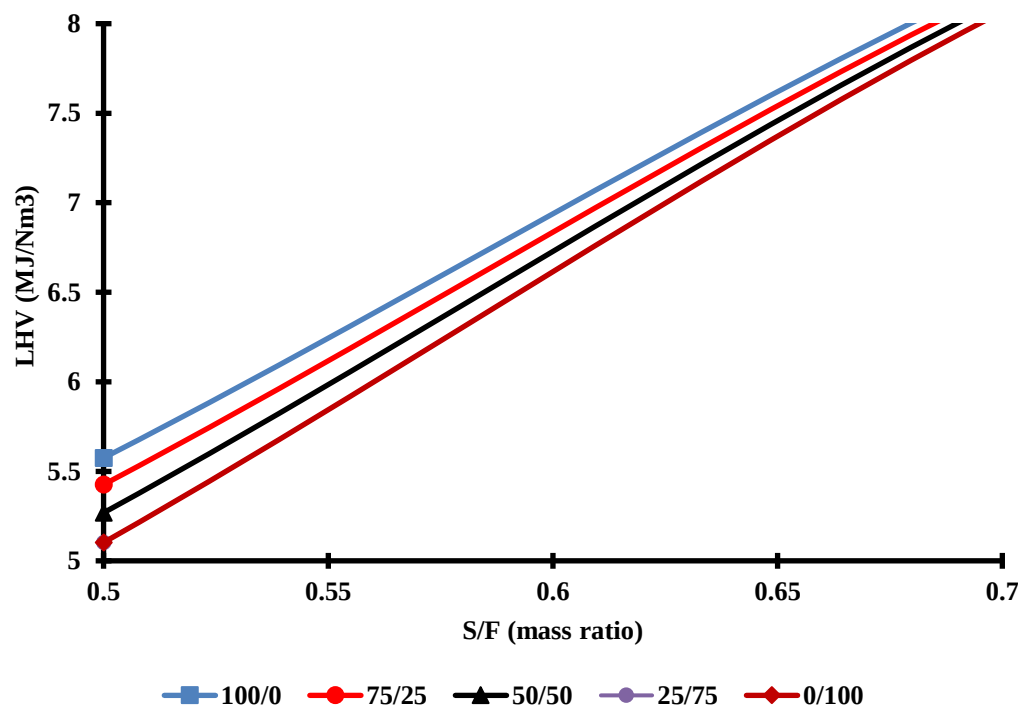


Figure 20 Effect of gasification steam to feed ratio and plastic blend on syngas at a gasification temperature 900 °C (PE/PP mass basis)

To perceive the effect of steam to plastic ratio along with the feedstock blending ratios,

Figure 20 was constructed representing the testing data. The study was conducted at the optimal gasification temperature (i.e., 900°C). As the polyethylene to polypropylene ratio enlarged, the heating value of the produced syngas was slightly enhanced. The impact of increasing the steam to plastic ratio was directly impacting the syngas heating value and the optimal was 1.25. Since there is no huge difference for the ratio of the blend, we decided to select PE/PP of 1:1 as the plastic feed in our model. The optimal blend was for the blends are 900°C , with S/P of 1.25 agreeing with our previous conclusion.

4.4.1.2 Sensitivity Analysis of Various parameters around WGS Unit

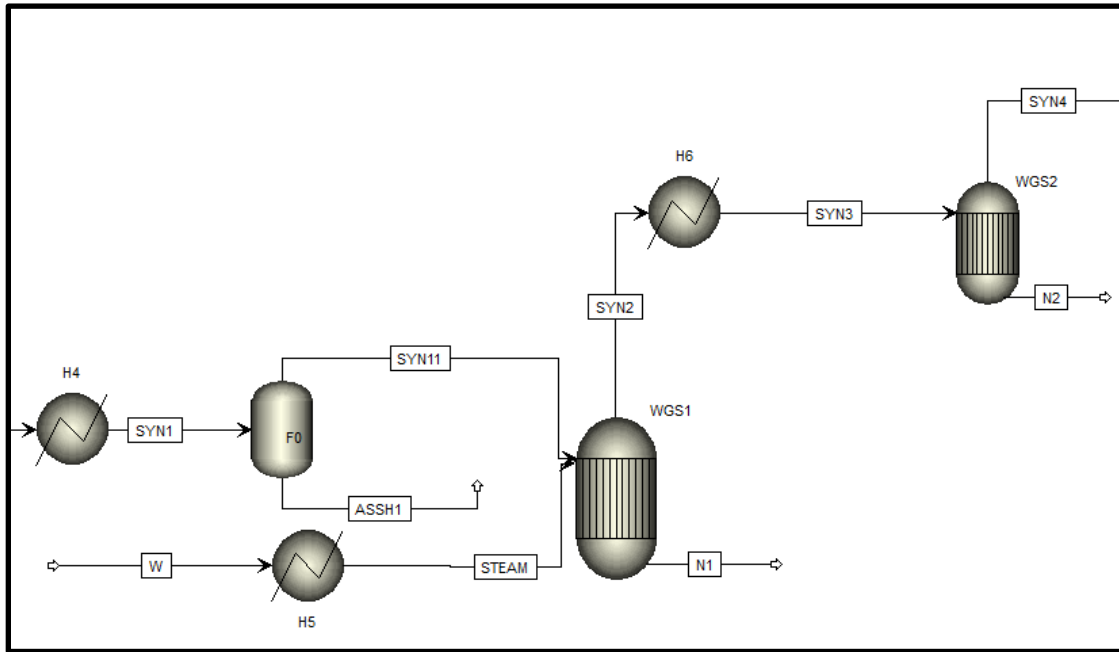


Figure 21 Scheme diagram for the WGS process

Water gas shift reactions are exothermic reactions, thus, increasing the cooling rate around the reactors will substantially enhance the conversion. **Figure 21** demonstrates the WGS process simulated via Aspen Plus. We prepared the WGS feed by cooling the gas mixture, then traces of ash were there and they were separated via normal flash drum. After that, the mixture along with specified steam to feed ratio were introduced to the first WGS reactor which is an equilibrium reactor (REquil). Through WGS reactions illustrated in **Table 6**, the carbon monoxide was simply converted to hydrogen and carbon dioxide. Then, another WGS reactor was modeled to grantee 99.9% conversion of CO to hydrogen. Finally, the products were prepared for AGR process via cryogenic cooling to 10°C.

a. The Effect of Steam on CO Conversion

WGS basically converts carbon monoxide to hydrogen and carbon dioxide. Thus, the main parameter to study is CO conversion. The injected steam has a strong effect on the

conversion which is represented by **Figure 22**. The optimal steam to inlet CO molar ratio was 1, which reveals a good agreement with stoichiometry.

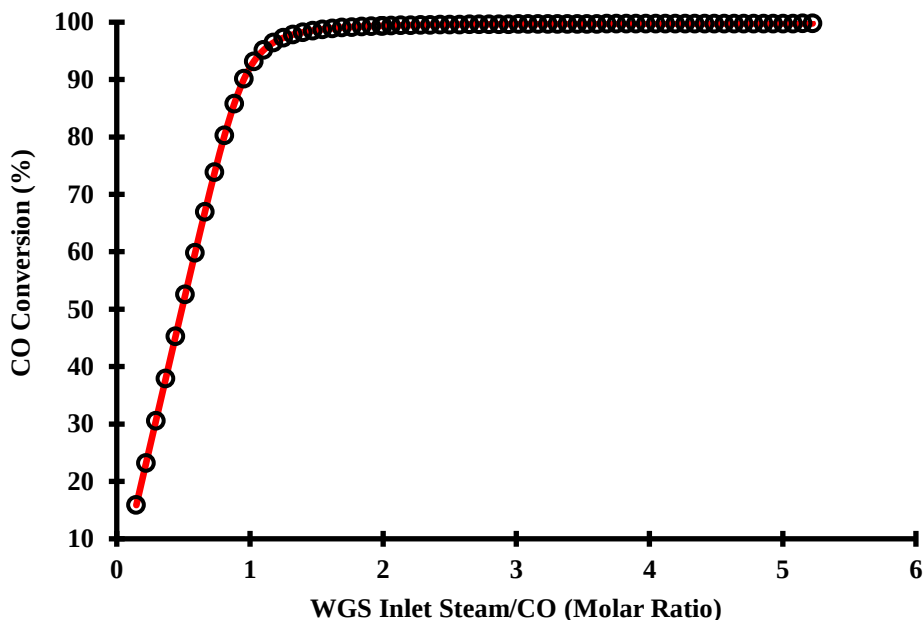


Figure 22 The effect of WGS steam inlet to the CO conversion for a mass ratio PE/PP of 0.5: 1; S/F of 1.25: 1

b. The Effect of Cooling Rate on CO Conversion

Cooling duty was significant parameter in simulating the WGS unit since the reactions are exothermic. Therefore, it had been studied seeking its impact on carbon monoxide conversion. The result revealed a substantial positive effect of cooling duty of WGS reactors. **Figure 23** illustrates the impact of first WGS reactor cooling rate on the carbon monoxide conversion. Since, the water gas shift reaction is exothermic, it was expected that, the equilibrium will shift to the right when the cooling duty increased. The remaining unconverted CO was reacted in the second WGS reactor (i.e., **Figure 24**). The effect of cooling rate in the second reactor is quite interesting. The conversion of carbon monoxide in the second WGS increased as the cooling rate increased, however, when the cooling rate

reached 50 KW, the conversion was decreased. The trend in the second WGS reactor is different than the first WGS, because in the second WGS reactor, the content of CO was very low, which reduced the equilibrium direction towards the products. Although, the conversion was high in WGS 1, however, it was crucial to ensure the highest conversion with reasonable cooling utility; thus, we selected 30 KW in the two reactors.

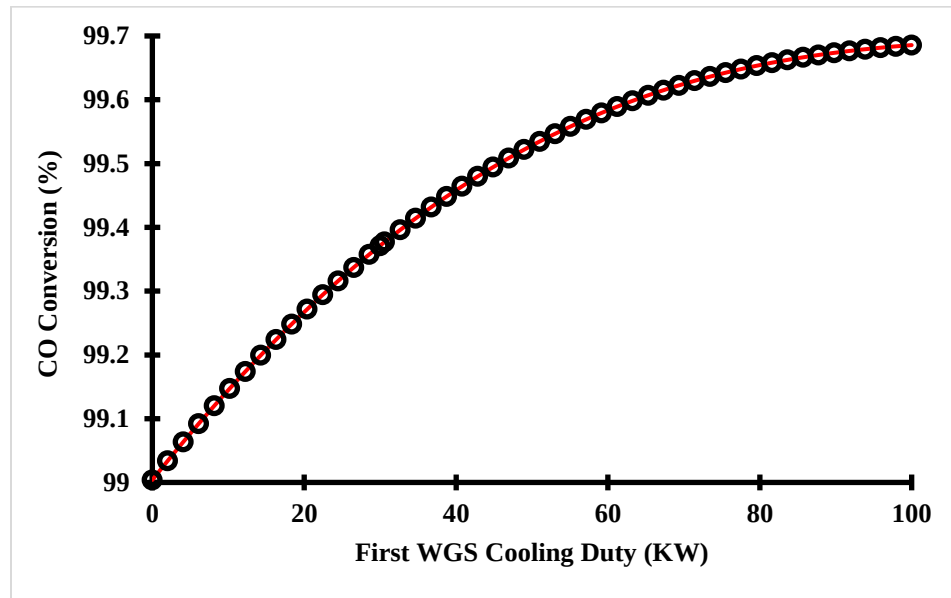


Figure 23 Effect of first WGS cooling duty on the conversion of carbon monoxide conversion for a mass ratio PE/PP of 0.5: 1; S/F of 1.25:1

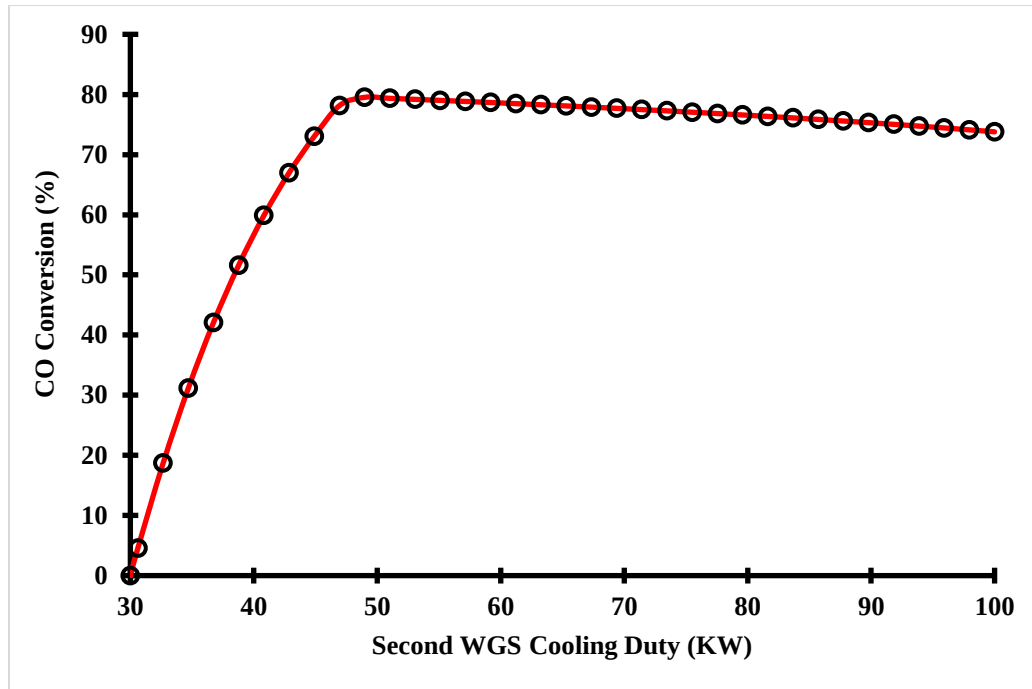


Figure 24 Effect of second WGS cooling duty on the conversion of carbon monoxide conversion for a mass ratio PE/PP of 0.5: 1; S/F of 1.25: 1

c. The Effect of Pressure on CO Conversion

For the WGS, we found that, the pressure has no effect on the outlet composition. Thus, the main effect will be in the gasifier and that would ultimately affect the Hydrogen production. Hence, rather than showing the comparative analysis on WGS, it would be more appropriate to show the net hydrogen production which is (39, 34 and 30 kg/s) at 1, 5 and 10 bar respectively. In the three models, we can see that the increase in gasifier pressure would decrease the net hydrogen production that can be also verified from the syngas composition in gasifier along with LHV at different pressures. The results indicated that, the overall Operation is preferable at low pressure in terms of H_2 production and syngas heating value. **Figure 25** reveals the impact of gasifier pressure on hydrogen production at the outlet of the unit of WGS.

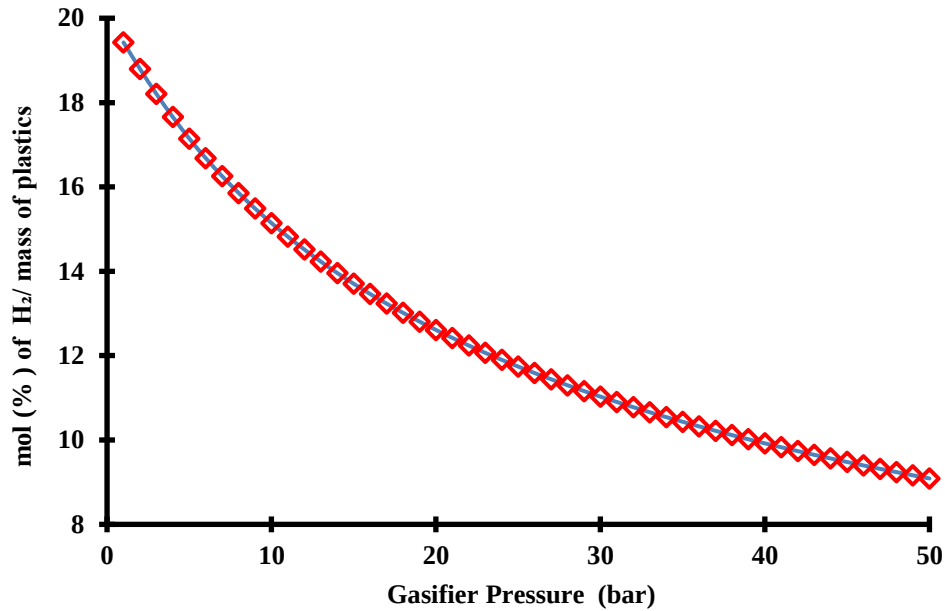


Figure 25 Effect of pressure in gasification and WGS units on the final produced amount of hydrogen

4.4.2 Analysis for Case 3 and Case 4

The main paramours in the two cases that ultimately impact the fuel production and energy consumption are the gasifier operational conditions, SMR feed flow rate, and temperature and pressure of methanol reactor. Hence, we tested those parameters and reported their effects on the key parametric results.

4.4.2.1 Impact of Gasifier Temperature and Pressure on Syngas Composition (Case 3)

We tested the impacts of plastic gasifier pressure and temperature on the syngas heating value which is represented by H₂/CO and SN. **Figure 26** and **Figure 27** show the effect of gasifier temperature and pressure on the stoichiometric number and hydrogen to carbon monoxide ratio. Increasing the gasifier temperature enhances the SN and H₂/CO. However, increasing the gasifier pressure decreases the SN and hydrogen to CO ratio. The high temperature promotes high quantity of hydrogen (higher contact of the gases with steam). Harris.et.al (2006), performed a study on the effect of gasifier temperature on the produced

gaseous concentrations, and he found that, as the gasifier temperature increases, CO_2 concentration reduced. Moreover, the concentration of CO and hydrogen increased [135]. According to Marek et al. (2012), increasing the pressure reduces the hydrogen concentration [136]. Our findings are in good agreement with the two experimental studies.

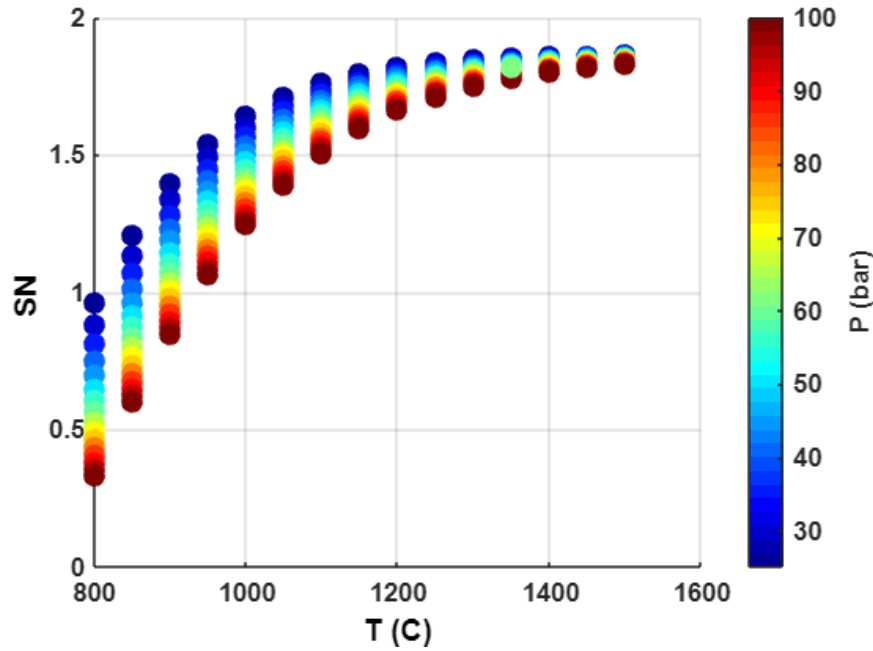


Figure 26 Impact of plastic gasifier temperature and pressure on the syngas SN ratio

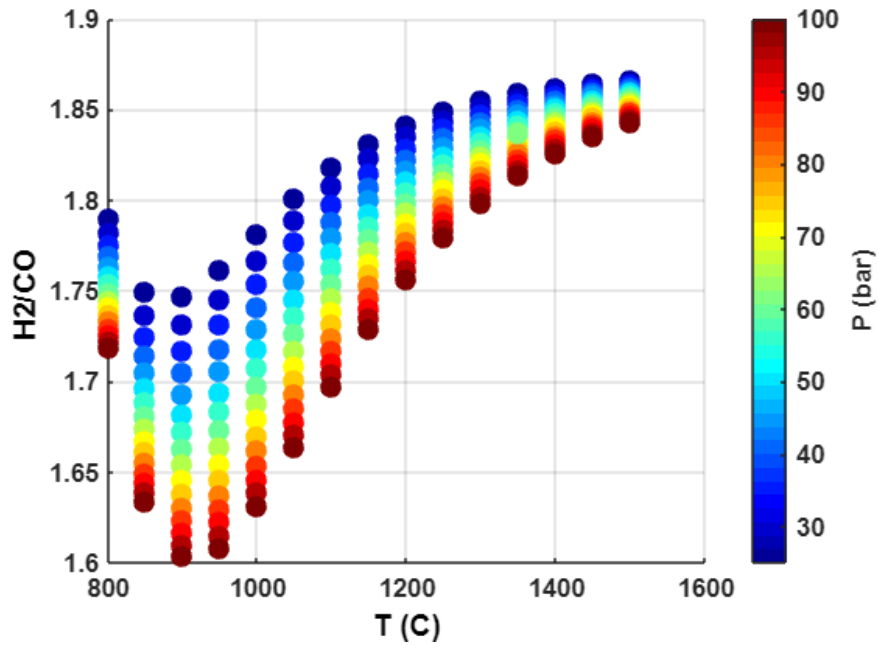


Figure 27 Impact of plastic gasifier temperature and pressure on H₂/CO ratio

4.4.2.2 Impact of Total SMR Flowrate on Hydrogen and Methanol Production (Case 4)

Case 4 involves two main processes that produce synthesis gas. Therefore, the blend ratio is a very significant factor affecting the whole design in terms of energy utilization and product quality. The plastic mass flow rate was constant with a value of 100 kg/h. Then, the SMR mass flow rate was tested with the control of steam to natural gas ratio (1.6 in mass basis). The first affected parameter is the total syngas flow rate at the inlet to methanol process. Obviously, increasing the SMR flow rate would increase the syngas production, however, the syngas heating value will be different. We tested the effect of SMR flow rate on the hydrogen composition and syngas molar flow rate (i.e., **Figure 28**). The hydrogen composition on the syngas rises as the SMR flow rate increases. The SMR process produces higher fraction of hydrogen than the gasification of the plastics. Thus, we perceive appreciable enhancement in the hydrogen fraction. Our selected total SMR flow

rate was 390 kg/h, which corresponds to 71% hydrogen composition in the total flow of syngas.

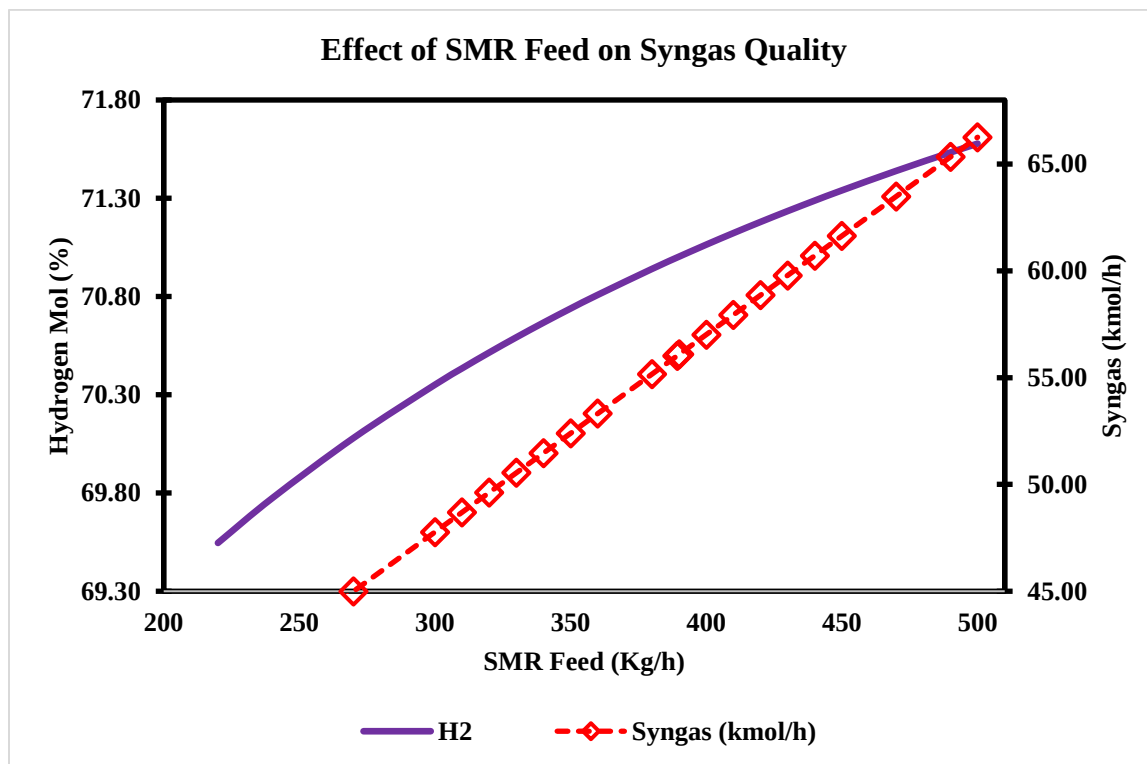


Figure 28 Effect of SMR total mass flow rate on the hydrogen composition and syngas molar flow rate at the inlet of methanol process

To visualize the impact of SMR flow rate on the final production rate of hydrogen, we plot the final produced hydrogen over molar flow rate of syngas at the inlet to the methanol process versus SMR total flow rate (**Figure 29**). Increasing the SMR flow rate has a slight impact on increasing the final amount of produced hydrogen. This increase is contributed to the enhancement of syngas heating value as SMR flow increases. The ratio of the final flow of hydrogen to the methanol inlet flow rate was 0.71. We additionally tested the purity of the produced hydrogen. We found a good improve in the purity. **Figure 30** shows a considerable improve of hydrogen purity when SMR flow rate increases. We achieved almost 95% purity of hydrogen using 390 kg/h as a total SMR flowrate.

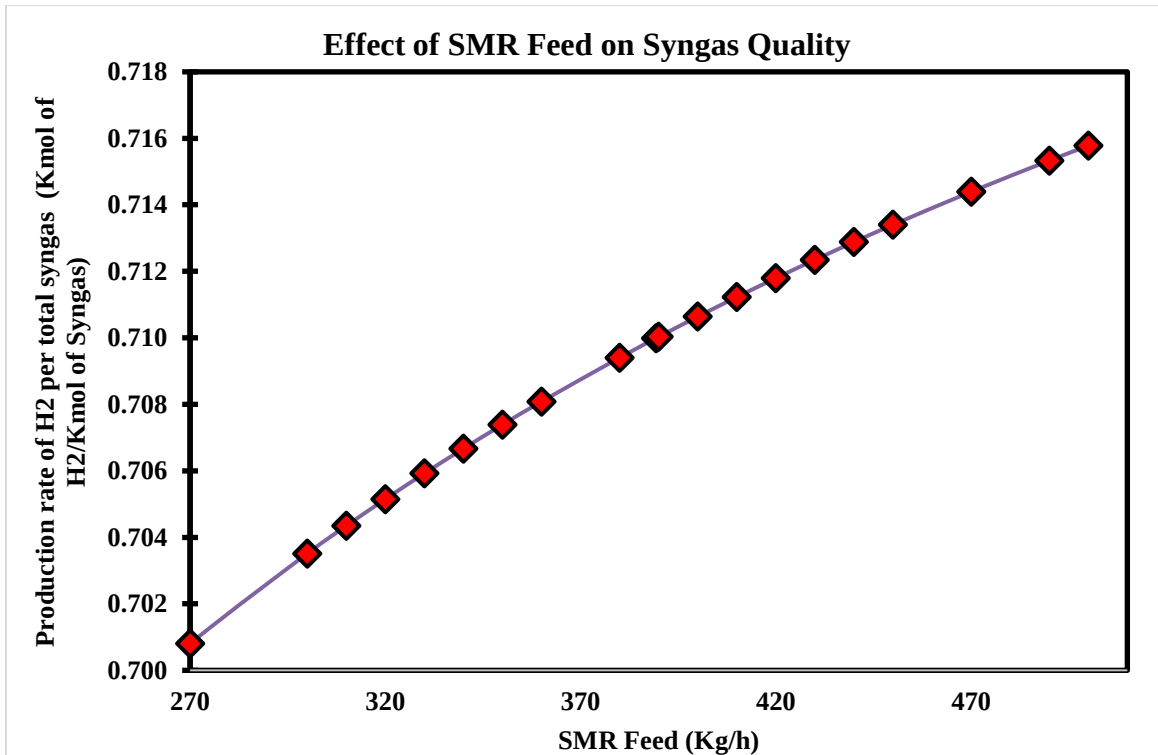


Figure 29 Impact of SMR total mass flow rate on the final hydrogen production rate per syngas at the inlet to methanol process

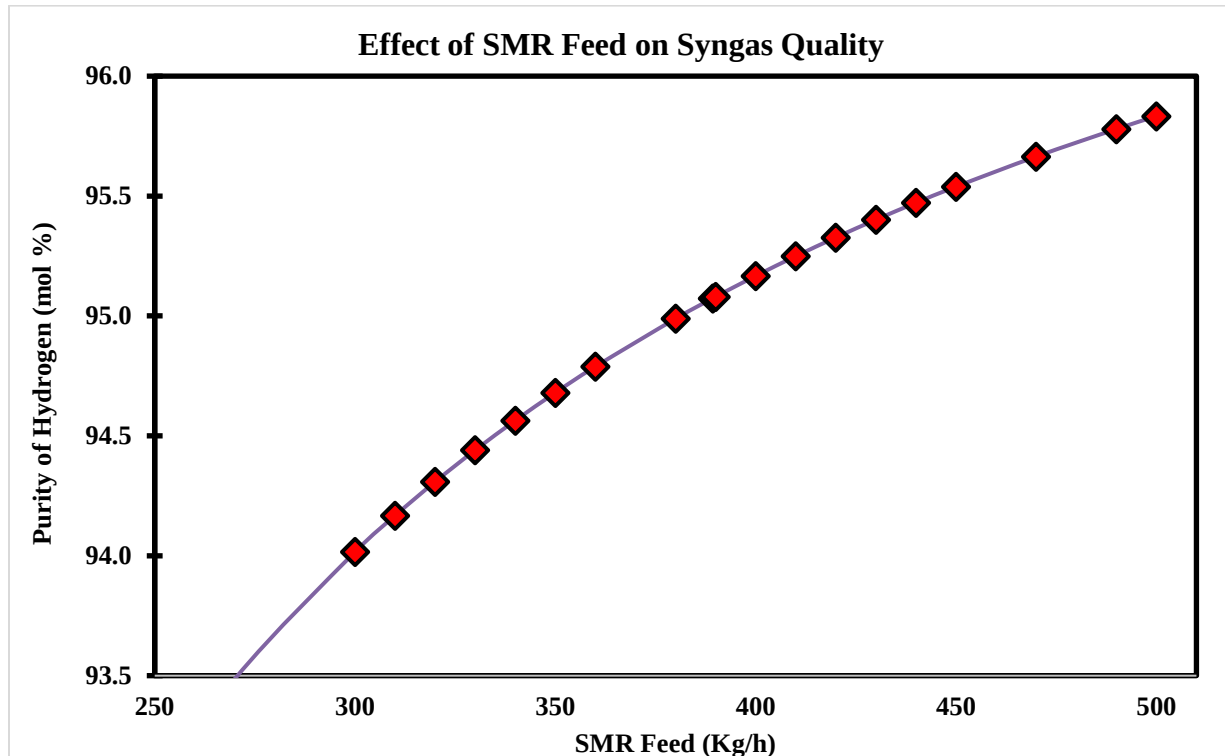


Figure 30 Effect of SMR total mass flow rate on the final purity of produced hydrogen

Another important parameter that is affected by changing SMR flow rate is methanol production rate. Understandably, increasing the SMR feed would increase the methanol production rate, thus, we divided the production rate of methanol over the total syngas stoichiometric number (i.e., SN). **Figure 31** displays the influence on SMR feed on methanol production deviating the obvious effect. The reason behind this noticeable enhancement is due to the increase in the CO₂ and H₂ compositions in the total syngas at the inlet of methanol process. The accomplished methanol production rate to SN at the corresponding selected SMR flowrate (i.e., 390 kg/h) was 6.5. Therefore, generally, increasing the SMR flowrate has a positive impact on key results in our alternative design. However, we selected 390 kg/h because of energy limitations. The goal is to exchange the heat from the plastic gasification and utilized it in heating the SMR feeding stream. Hence, it is considered the optimal flowrate, and it is corresponding to a mass ratio of NG: plastics of 1.5. Moreover, the further increase in the SMR has small impacts on the normalized hydrogen and methanol production rates.

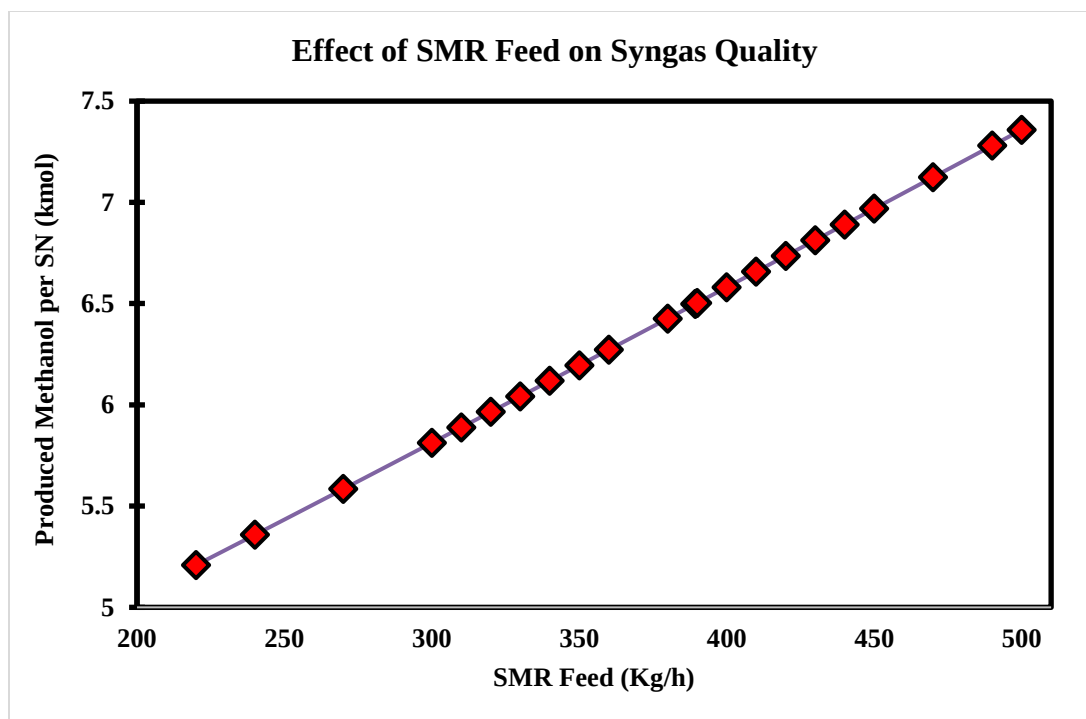


Figure 31 Impact of SMR total mass flow rate on the production rate of methanol per mixed syngas SN stoichiometric number

4.4.2.3 Effect of Temperature and Pressure of Methanol Reactor on its Production Rate (Case 3)

The temperature of the methanol synthesis reactor is an important factor, and its effect is a combined effect. Increasing the temperature enhances the kinetics however, the equilibrium constants will decrease since the reactions are exothermic one. The equilibrium is slightly superior to the kinetics; hence, we perceive a decrease in the methanol production rate. **Figure 32** illustrates the impact of PFR temperature (i.e., it is selected to be the same as the inlet temperature) on the methanol production rate. We selected the inlet temperature to the methanol synthesis reactor as 290 °C because we were limited to the model conversion. Additionally, the effect is very minimal. **Figure 33** demonstrates the effect of the pressure of the reactor on methanol production rate. The impact of the pressure is a positive impact, however, slight increase in the production rate was perceived.

Therefore, we chose 25 bars as the pressure of the reactor. Moreover, the results illustrated in **Figure 26** limited the further increase in the pressure not to need additional compression utility with special reactor design.

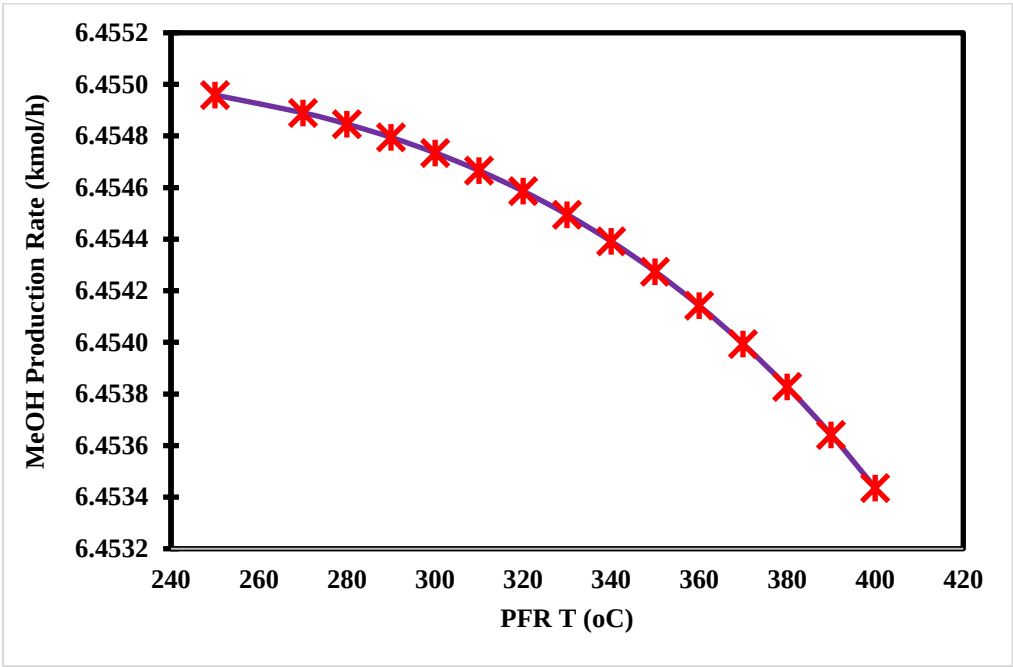


Figure 32 Impact of methanol reactor temperature on its production rate

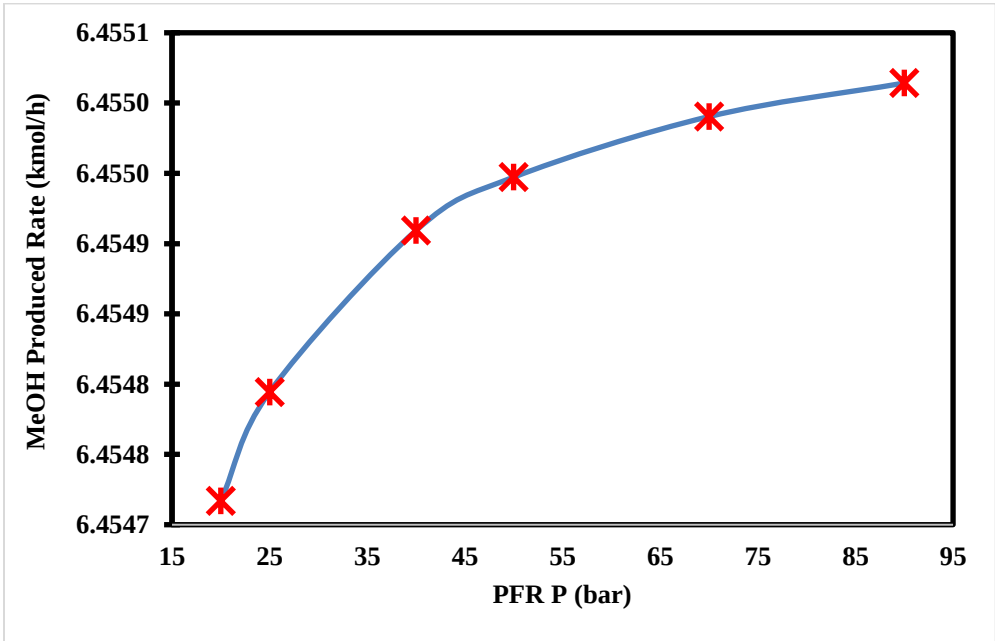


Figure 33 Impact of methanol reactor pressure on its production rate

4.5 Economic Analysis

4.5.1 Hydrogen Production Model (Case 1 and Case 2)

To perform the economic analysis for the two designed cases, previous studies were the data source for initial plant cost estimation. The fixed capital investment was evaluated based on individual cost estimation of the processes depending on the process capacity and CEPCI. **Equation 9** was the main equation for estimating the CAPEX. Certain assumptions were taken in estimating the operating expenditures. The maintenance, working capital, and land and salvage were estimated based on the fixed expenditures. The labor cost was calculated based on **Equation 11**. Then, the administration cost was evaluated from the labor cost. We selected the exponent x to be 0.6. We estimated the utility cost based on the utilities of each unit, then, calculating the price of each utility depending on the type of the duty. The reference for that calculation was Donald E. Garrett book [137]. The taxation rate was considered and selected to be 15%. To construct the plant cash flow diagram, we chose the plant life of 30 years with three daily shifts with stream factor of 0.95. The economic assumption summary is given in **Table 19**. The assumptions were in good match of previous studies Usama Ahmed (2020) [95] and Richard et al. (2009) [138].

Table 19 Economic assumptions

Economic Assumptions	
Waste Plastics	Available Free of Charge
Natural Gas (€/GJ)	5
Cooling Water price €/ton	0.01
Waste Disposal (€/ton)	10
Plant construction time (Year)	3
Plant Life (Years)	30
Maintenance (% from Equipment cost)	2
Offsite Unit and Utilities (% from Equipment cost)	25
Contingency Cost (% from Equipment cost)	15
Permitting (% from Equipment cost)	5
Discount rate	0.08
Administration (% from Labor Cost)	30
Labor Cost €/Person	45000
Stream factor	0.95
Daily Shifts	3
Land and Salvage (fraction of FCI)	1/9
Working Capital (% of FCI)	10
Taxation Rate (%)	0.15
Ratio of recycling methanol solvent respectively	0.01 & 0.005
Price of Methanol (€/ton)	600
Price of Boiling water M€/ton	2.03
x	0.60
CEPCI (2021)	620

4.5.1.1 Estimation of CAPEX and OPEX

The fixed capital expenditure (CAPEX) and the operational expenditure (OPEX) are the two crucial parts for estimating the required total investment for any project. The total investment is impacted by various variables such as capacity of the plant, the used raw materials, the operational time, and the process efficiency. The fixed CAPEX predominantly includes the equipment and plant facilities costs. In this study, we used the power law to estimate the CAPEX with capacity factor (x) of 0.6 using the concept of Chemical Engineering Plant Cost Index (CEPCI). **Table 20** demonstrates the CAPEX cost summary calculating some essential parameters (i.e., total investment cost and TIC). We can perceive a difference in the TIC for the two studied cases due to the variation in the process configuration and the used feedstock type. The deduced total investment cost (FCI) in terms of M€ for the two cases was found to be 3.795, and 4.457 respectively. The FCI for the alternative case is larger than the base case since we introduced new process (i.e., SMR), the overall capacity increased. The TIC represents the total investment cost per hydrogen production capacity in ton. We found lower TIC for the alternative case by 23% indicating the economic efficiency of the alternative case in terms of CAPEX.

Table 20 CAPEX cost summary for the two studied cases for hydrogen production

Equipment	Case 1 € (10³)	Case 2 € (10³)
SMR Unit	0	128
Acid Gas Removal Unit	1339	1624
Syngas processing unit	646	690
Solid Handling Facility	522	522
Gasification Unit	110	110
Equipment and Installation Cost	2617	3074
Offsite Unit and Utilities (25% of Installation Cost)	654	768
Contingency Cost (15% of Installation Cost)	393	461
Permitting (5% of Installation Cost)	131	154
Total Investment Cost	3795	4457
TIC per ton of H ₂ M€/ton	76.53	59.25

On the other hand, the operational cost of the project is represented by OPEX, which is classified in to two different categories. The two categories are the fixed OPEX and variable OPEX. The fixed OPEX involves the maintenance, labor, and administrative costs, where the variable OPEX comprises the fuel, catalysts, waste disposal, and boiler feed water costs. **Table 21** shows the OPEX summary for the two designed cases. The total OPEX in K€/Year for the two cases was found to be 1390 and 1469 respectively. The alternative case had higher OPEX than the base case by 5.7% due to the capacity difference. However, once we calculated the OPEX in K€/ ton of produced hydrogen, the OPEX for the alternative case was less by 30%. This amount of OPEX cost reduction points the overall economic efficiency for the alternative case.

Table 21 OPEX cost summary for the two modeled cases: hydrogen production

Cost Sector/ Designed Case	Case 1 € (10³) / Year	Case 2 € (10³) / Year
Maintenance Cost (2% of Equipment and Installed Cost)	52.3	61.5
Labor Cost	459.4	472.9
Administrative, support & overhead cost	137.8	141.9
Total Fixed Manufacturing Cost	649.6	676.2
Natural Gas	0.0	16.5
WGS Catalyst	16.6	18.0
Reforming Catalyst	0.0	0.5
Solvent	39.0	57.8
Waste disposal	7.1	7.1
Utility Costs	677.9	693.2
Total OPEX/Year	1390.0	1469.3
Total OPEX/ton H ₂	3.4	2.3

4.5.1.2 Comparison of Hydrogen Costs with the Literature

This section demonstrates the hydrogen production cost with respect to the total investment cost per amount of hydrogen produced. Additionally, it provides the cash flow diagram for the base and alternative case. Furthermore, it gives the literature validation and comparison between various processes. **Figure 34** reveals the hydrogen production cost in €/kg, and the TIC in M€/year for the two cases.

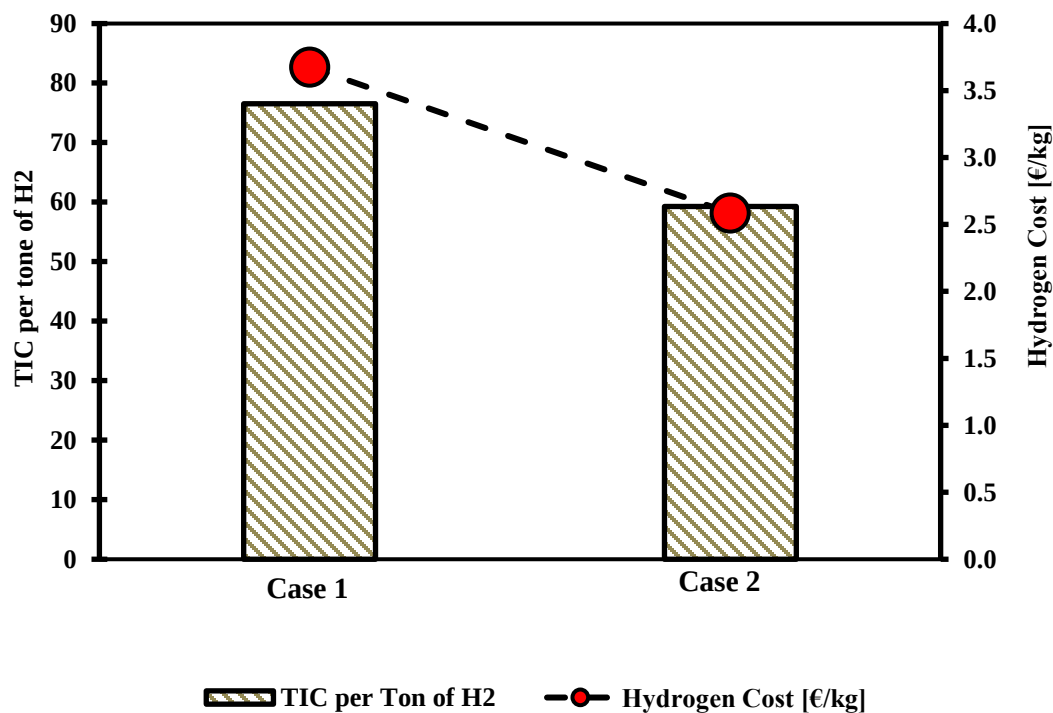


Figure 34 The TIC per ton and hydrogen cost for the two cases

Hence, the two parameters indicate how the process is efficient in terms of capital and operational cost. We can perceive that; the alternative case is much more efficient than the base case. The cash flow diagram was investigated and provided as **Figure 35**. The cash flow return on investment was higher for the alternative than the base case by 52%. Additionally, the net present value (NPV) was greater by 78% compared to the base case, where the present value ratio (PVR) was higher by 45%. We included the dominance of alternative case in terms of economic analysis than the base case.

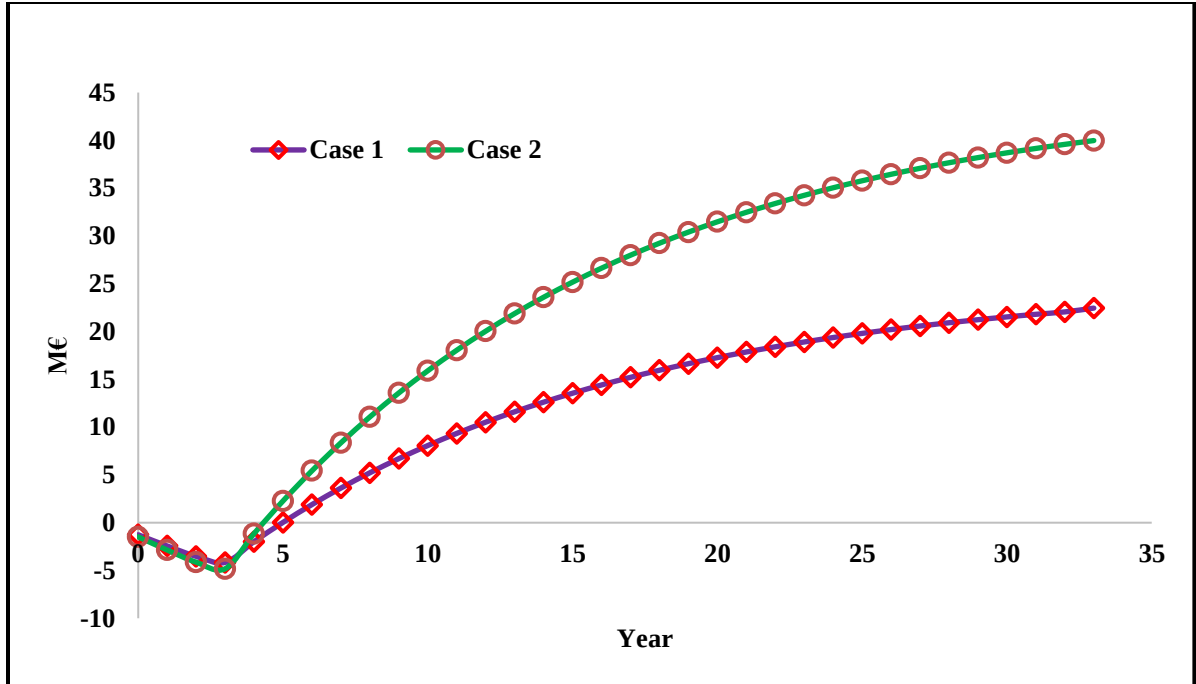


Figure 35 Cash flow diagram for the two cases to produce hydrogen from plastics: base case and methane reforming case.

To validate our economic analysis and to demonstrate the effect of feedstock on the hydrogen production cost, we compared our results with the literature studies [139] [140] (i.e., **Figure 36**). The solar and photovoltaic electrolysis of water has the highest hydrogen cost (it is considered green; however, it consumes more energy). Biomass, coal and heavy oil can produce hydrogen with lower cost than solar process, however, they still have higher cost due to the complexity of their feedstock. The cost can vary from study to another, however the range from 5-8 €/kg [141]. Our designs are pretty like the SMR process; however, the alternative case is more competent.

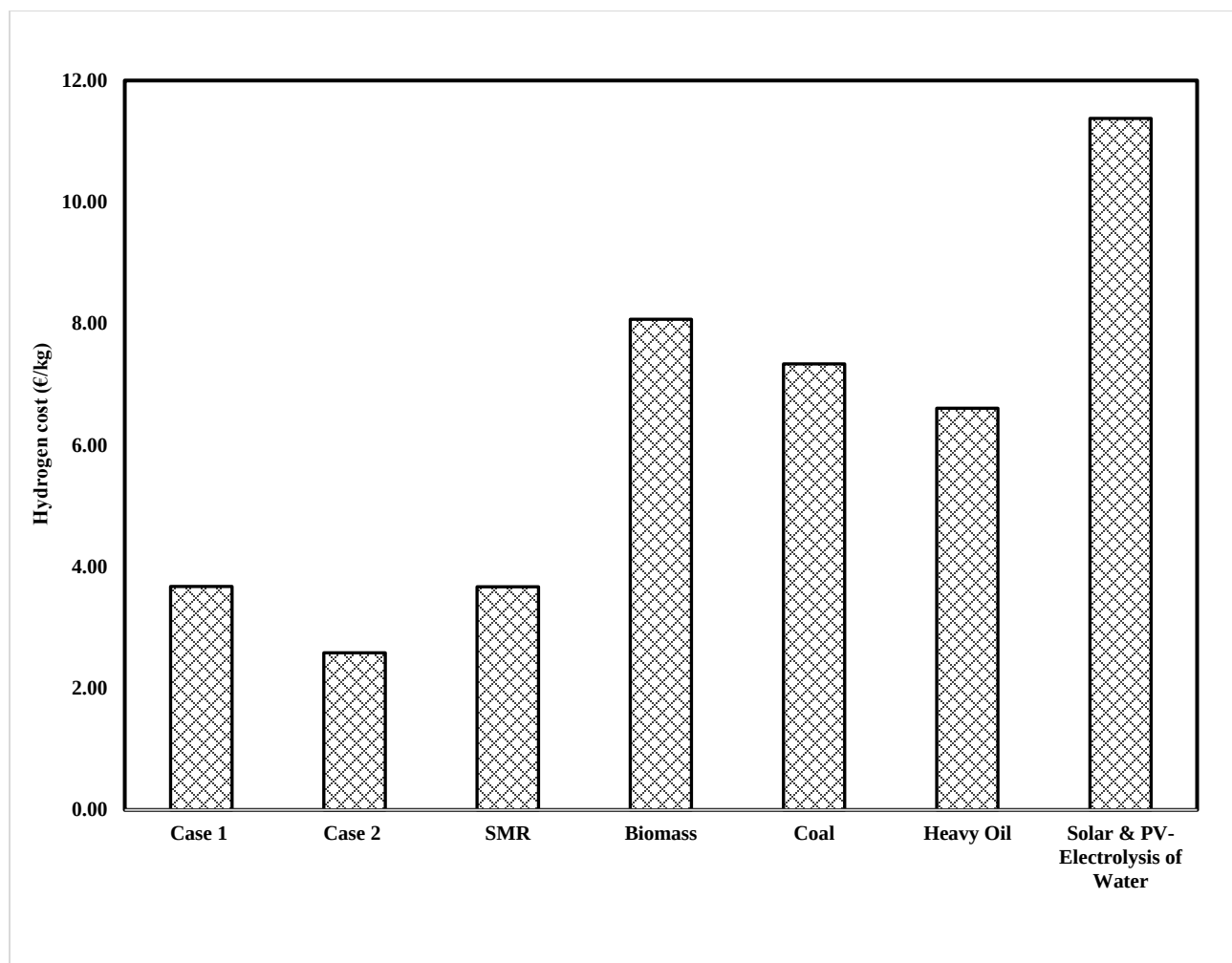


Figure 36 Hydrogen production cost on our study compared with previous studies

4.5.2 Dual Hydrogen and Methanol Production Model (Case 3 and Case 4)

4.5.2.1 Estimation of CAPEX and OPEX

The main two expenditures are the fixed capital expenditure (CAPEX) and the operational expenditure (OPEX). Several factors affecting the two expenditures which are the process efficiency, operational time, the raw materials, and the plant capacity which were all selected and illustrated in the previous sections. Equipment and installation cost were deduced from previous studies. The cost of equipment and installation for the gasification was based on study performed on entrained gasifier; the feed was biomass [142]. The

methanol synthesis previous cost estimation was based on Graaf.et.al kinetics in estimating the methanol synthesis unit price [143]. The estimation of the other units was according to Usama.et.al (2020)[93]. **Table 22** exhibits the CAPEX summary and the total investment cost per ton of the produced fuel. The two cases have different costs due to the difference in the capacity and feedstock compositions. Case 3 has no SMR, however, case 4 has no WGS. The total investment cost for case 4 is larger than case 3 by 13.4%. It is attributed to the larger feedstock in case 4 than case 3. Nevertheless, the TIC for case 4 is lower than case 3 by 72.5%. Hence, case 4 is more efficient than case 3 in terms of capital expenditures.

Table 22 The capital expenditures cost summary for hydrogen and methanol production

Unit	Case 3 € (10 ³)	Case 4 € (10 ³)
SMR Unit	0	275
Acid Gas Removal Unit	1096	1177
Syngas processing Unit	108	0
Solid Handling Facility	522	522
Gasification Unit	110	110
Methanol Synthesis Unit	969	1842
Equipment and Installation Cost	1836	2084
Offsite Unit and Utilities (25% of Installation Cost)	459	521
Contingency Cost (15% of Installation Cost)	275	313
Permitting (5% of Installation Cost)	92	104
Total Investment Cost	2663	3021
TIC per ton of H ₂ and CH ₃ OH M€/ton	433	119

The operating expenditures are classified to fixed and variable OPEX. The fixed OPEX includes the labor, maintenance, and administrative costs. The variable OPEX involves the catalysts expenses, the feedstock price, the solvent price, and waste disposal cost [137].

Table 23 shows the summary of the operating expenditures for the two cases. The total fixed manufacturing cost for case 3 and case 4 were 0.504 and 0.526 M€/Year respectively. The total OPEX in M€/Year for case 3, and case 4 were 0.839 and 1.0322 respectively. Case 4 had higher OPEX than case 3 by 23%. The alternative case requires higher operating expenses because the plant capacity is higher. A proper representation parameter for OPEX is to normalize the total operating cost by the production rate of the fuel. The alternative case cost in M€ per ton of fuel was lower than case 3 by 70%. It proves the superiority of case 4 than case 3 in terms of the lower consumption of operating expenditures relative to the fuel production.

Table 23 The operating expenditures summary for the two cases for hydrogen and methanol production

Cost Sector/ Designed Case	Case 3 € (10³)	Case 4 € (10³)
Maintenance Cost (2% of Equipment and Installed Cost)	56.1	78.5
Labor Cost	344.7	344.7
Administrative, support & overhead cost	103.4	103.4
Total Fixed Manufacturing Cost	504.2	526.7
Natural Gas	0.0	59.0
WGS Catalyst	2.8	0.0
Reforming Catalyst	0.0	1.1
Solvent	128.9	76.4
Waste disposal	7.0	7.1
Utility Costs	192.2	325.5
Total OPEX/Year	839.1	1032.2
Total OPEX/ton H ₂ & CH ₃ OH	16.4	4.9

4.5.2.2 Comparison of Fuel Costs with the Literature

This section demonstrates the fuel production cost (hydrogen and methanol) and total investment cost per fuel production rate. Additionally, the cash flow diagram is constructed for the base and alternative cases. Moreover, it will validate the fuel production cost and compare it with the literature. **Figure 37** reveals the TIC in M€/year for the two designed

cases, and the fuel production cost in €/kg, and the TIC in M€/year. The dual production cost of methanol and hydrogen was lower in case 4 than case 3 by 0.277 €/kg, which is less than the half. We recommend case 4 than case 3 to reduce the production cost of methanol and hydrogen.

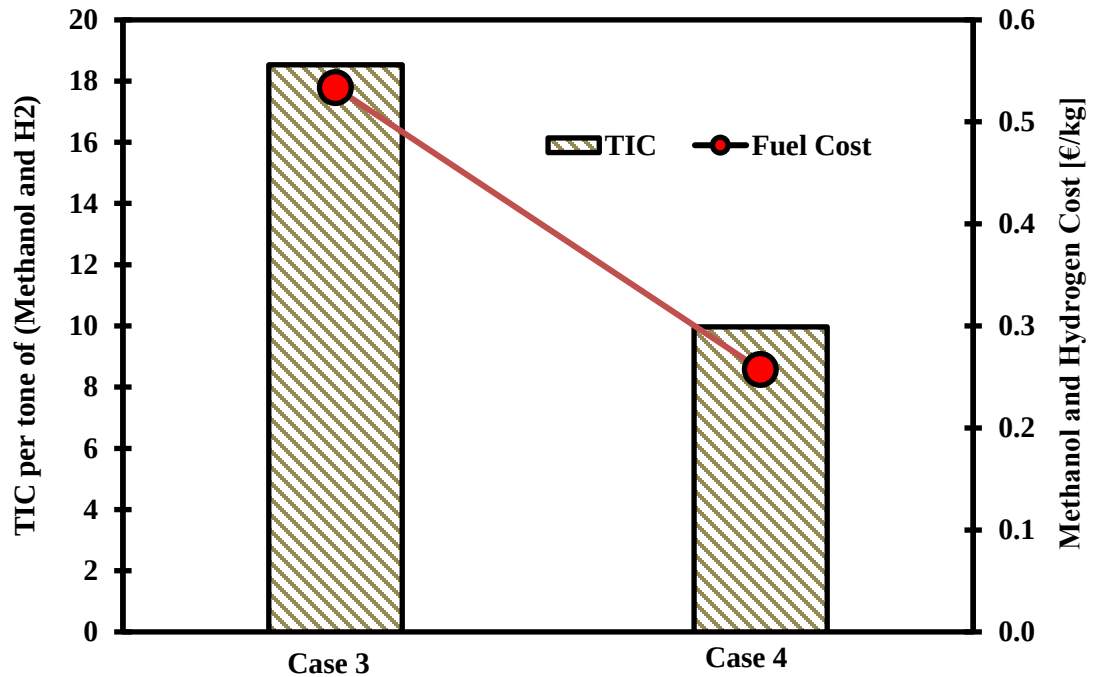


Figure 37 The TIC per ton of methanol and hydrogen for case 3 and case 4

To evaluate and construct the cash flow diagram, we divided the total investment cost equally divided for three years. The revenue was calculated based on the production rate of hydrogen and methanol correspondingly multiplied by the average price of hydrogen and methanol. The depreciation was considered and assumed to be 10% of the total investment cost. **Figure 38** reveals the cash flow diagram for case 3 and case 4. Clearly, the cash flow for case 4 is much superior to case 3. The revenue was greater in case 4 than case 3 by 3.526 M€/year. The net present value (NPV) was also evaluated for case 3 and

case 4; 2.734 and 26.201 respectively. The present value ratio (PVR) was also calculated for the two cases which were 1.614 and 5.301 respectively. Those calculations clearly indicate the significant improvement in the economic efficiency of the alternative case than case 3.

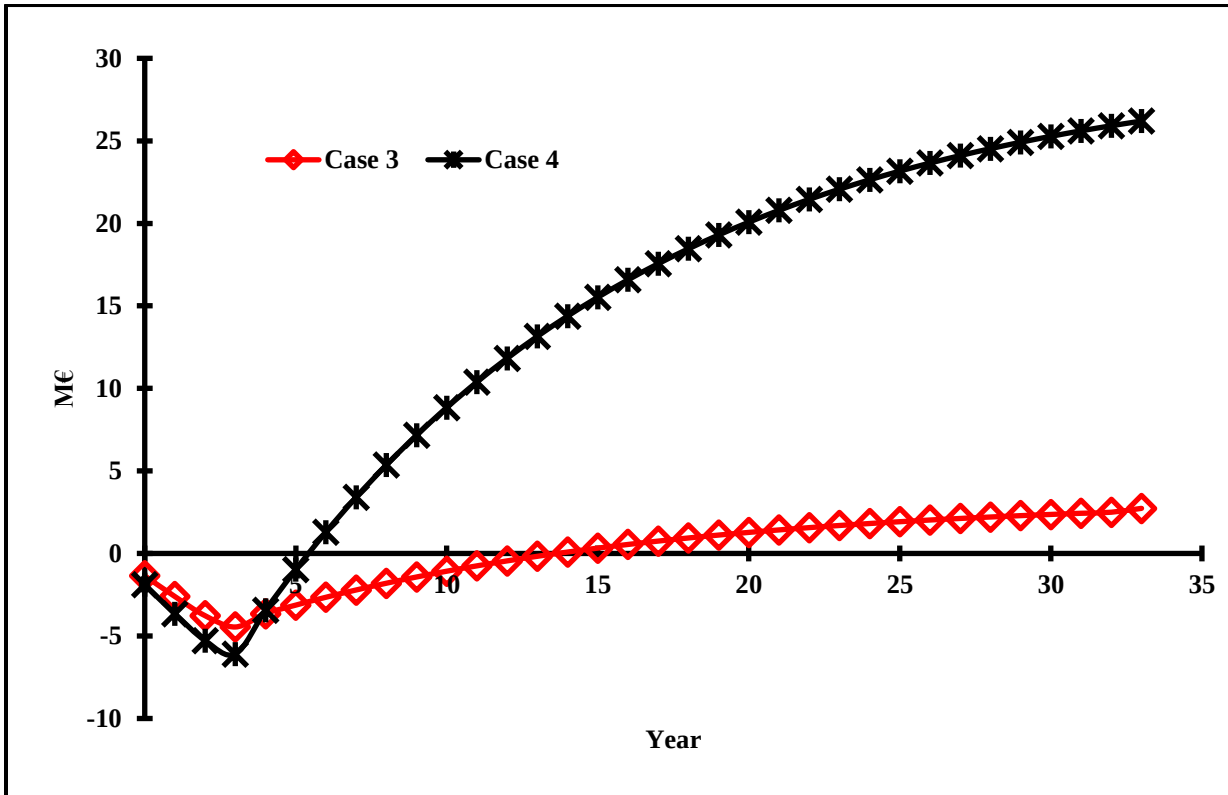


Figure 38 Cash flow diagram for case 3 and case 4 for methanol and hydrogen production

We compared the fuel cost per production rate for our model with the previous design in producing simultaneous hydrogen and methanol. Usama Ahmed (2020) studied the dual production of methanol and hydrogen. The study performed the economic analysis and found that, the production cost of the two fuels (H_2 and CH_3OH) in €/kg were 0.28 and 0.23 for case 3 and case 4 respectively [144]. **Figure 39** demonstrates the total cost of the two fuels from plastics (in this study) and from coal (previous study). Case 4 from plastics

is comparable with the one from coal. Case 3 has higher production cost than that from coal. Therefore, producing the methanol and hydrogen from plastics is feasible.

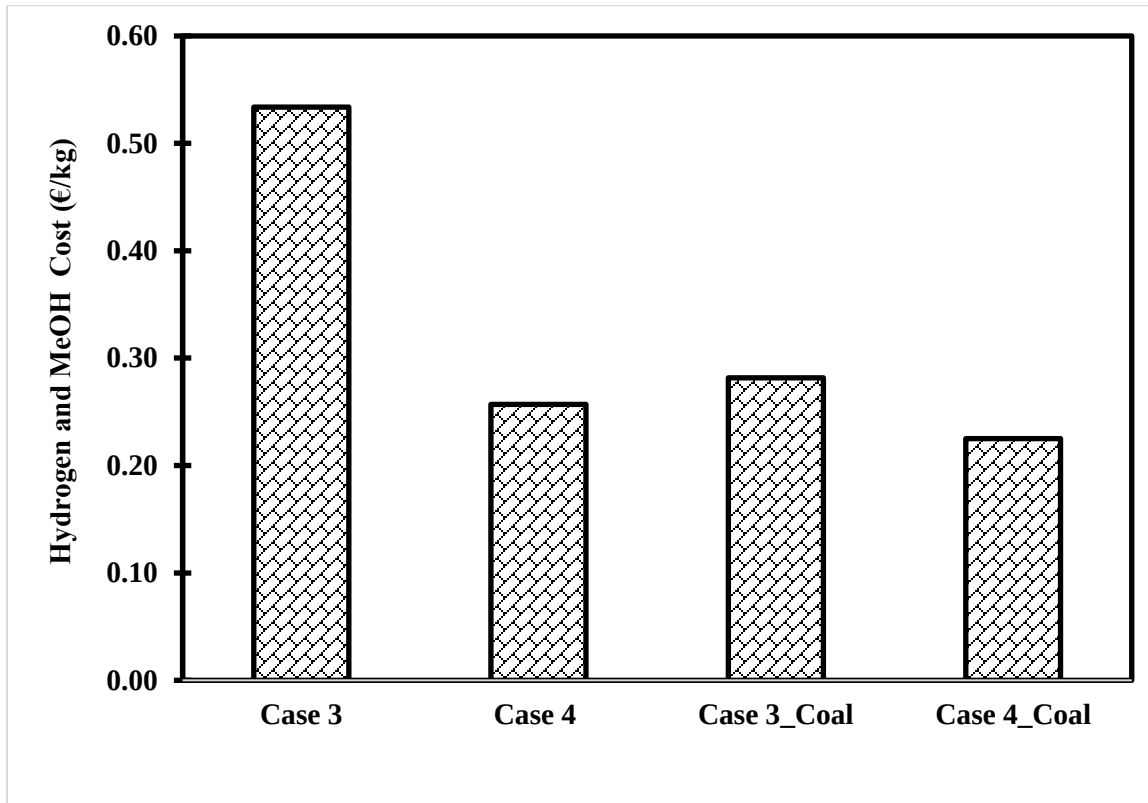


Figure 39 Dual methanol and hydrogen production costs on our study compared with previous studies

Two developed cases were modeled for simultaneous hydrogen and methanol production. Some sensitivity analysis was performed testing some parameters in case 3 and case 4 to properly select the optimal design conditions. To evaluate the model performance, we analyzed the two cases in terms of product heating value, energy performance, carbon dioxide specific emissions, and cost analysis. We expect case 4 to be superior to case 3 in the whole comparison aspects because it produces higher LHV synthesis gas with a huge reduction in the energy consumption which would result in cost reduction.

4.6 Conclusion

The production of hydrogen and methanol was accomplished from waste plastics. The selected plastics were polyethylene and polypropylene. We performed two different studies. The first study was on hydrogen production in two different technologies. The first technology (case 1) involved steam gasification only to produce hydrogen. The second technology (case 2) involved another syngas producing process which is SMR (i.e., integrating steam gasification with SMR). The second study was like the first study; however, we produce hydrogen and methanol simultaneously (i.e., case 3 and case 4 respectively).

The results from the first study revealed the following. When 100 kg/h of the plastic fed with 251 kg/h of steam, 50 kg/h of hydrogen produced (case 1). The sensitivity analysis for steam gasification and WGS units was performed seeking the optimal operating conditions. The optimal conditions for the gasifier were at 900 °C and atmospheric pressure with steam to plastic ratio of 1.25. The first case (case 1) was feasible and efficient in producing hydrogen with low CO₂ specific emissions. However, there was a huge energy consumed in cooling the syngas prior to WGS after the gasification. Therefore, a more feasible technology (i.e., case 2) had been implemented to utilize that energy by integrating the steam gasification and natural gas reforming. The case 2 is technically more efficient than case 1, however, we needed it to prove the competence in terms of energy consumption and cost reduction. Hence, we conducted the whole analysis for the two technologies likewise. The percentage errors were performed with respect to the base case. The results revealed that, the H₂/CO ratio of the total produced syngas for the two cases were 1.86 and 2.23 respectively, which is 19.78% higher. Thus, the net heating value for

case 2 was higher than case 1 by 6.0%. The normalized hydrogen production per total feedstock was higher in case 2 than case 1 (i.e., 50 and 52.2 % respectively). Additionally, the overall process efficiency was greater in case 2 when compared to case 1 by 6.43%. The second technology also superior to the first one in reducing CO₂ specific emissions by 1.0%. The economic analysis for the second case revealed appreciable reduction in the total investment per feed (TIC) and in the hydrogen production cost than the first case 1 by 23% and 30% respectively.

In the second study (i.e., case 3 and case 4), the results indicated the following. The gasifier pressure and temperature enhanced syngas heating value. Additionally, the impact of SMR total flowrate on the normalized methanol, and hydrogen production rate was studied. The process efficiency for the two cases was 71.3 and 80.3% respectively. The normalized production rate of methanol and hydrogen was superior in case 4 than case 3 (i.e., 65.6% and 3.0% respectively). The fuel production cost per its production rate was calculated to be 0.53 and 0.26 for case 3 and case 4 respectively. The whole analysis ensured effectiveness of the integrated model (case 4) than the classical one. Moreover, the economic analysis suggests a feasibility of plastic conversion to simultaneous production of hydrogen and methanol. We suggest investigation different plastic blends to perceive the effect in the design, energy consumption and cost reduction. It will contribute to enhance the plastic thermal recycling because the plastic classification is challenging in the plastic recycling journey. Additionally, we recommend studying the production of several other fuels (i.e., ethanol and DME) from waste plastics.

References

- [1] “Global Energy Outlook 2021: Pathways from Paris.”
<https://www.rff.org/publications/reports/global-energy-outlook-2021-pathways-from-paris/> (accessed Nov. 07, 2021).
- [2] M. Puig-Gamero, J. Argudo-Santamaria, J. L. Valverde, P. Sánchez, and L. Sanchez-Silva, “Three integrated process simulation using aspen plus®: Pine gasification, syngas cleaning and methanol synthesis,” *Energy Conversion and Management*, vol. 177, pp. 416–427, Dec. 2018, doi: 10.1016/J.ENCONMAN.2018.09.088.
- [3] “Energy and Climate Policies beyond 2020 in Europe-Overall and selected countries,” 2015.
- [4] I. Renewable Energy Agency, “Global Energy Transformation: A Roadmap to 2050 (2019 Edition),” 2019, Accessed: Nov. 07, 2021. [Online]. Available: www.irena.org
- [5] A. Okunola A, O. Kehinde I, A. Oluwaseun, and A. Olufiropo E, “Public and Environmental Health Effects of Plastic Wastes Disposal: A Review,” *Journal of Toxicology and Risk Assessment*, vol. 5, no. 2, Apr. 2019, doi: 10.23937/2572-4061.1510021.
- [6] R. Verma, K. S. Vinoda, M. Papireddy, and A. N. S. Gowda, “Toxic Pollutants from Plastic Waste- A Review,” *Procedia Environmental Sciences*, vol. 35, pp. 701–708, Jan. 2016, doi: 10.1016/j.proenv.2016.07.069.
- [7] R. C. Thompson, C. J. Moore, F. S. V. Saal, and S. H. Swan, “Plastics, the environment and human health: Current consensus and future trends,” *Philosophical Transactions of the Royal Society B: Biological Sciences*, vol. 364, no. 1526, pp. 2153–2166, Jul. 27, 2009. doi: 10.1098/rstb.2009.0053.
- [8] J. R. Jambeck *et al.*, “Plastic waste inputs from land into the ocean,” *Science* (1979), vol. 347, no. 6223, pp. 768–771, Feb. 2015, doi: 10.1126/science.1260352.
- [9] Woldemar d’Ambrières, “Plastics recycling worldwide: current overview and desirable changes,” 2019.
- [10] Basil D. FavisPierre Le Corroller, “US9670344B2 - Polymeric material and process for recycling plastic blends - Google Patents,” 2011

- [11] M. Mohammadzadeh, "Characterization of recycled thermoplastic polymers."
- [12] Raju Francis, *Recycling of Polymers: Methods, Characterization and Applications* | Wiley. 2016.
- [13] N. Singh, D. Hui, R. Singh, I. P. S. Ahuja, L. Feo, and F. Fraternali, "Recycling of plastic solid waste: A state of art review and future applications," *Composites Part B: Engineering*, vol. 115, pp. 409–422, Apr. 2017, doi: 10.1016/j.compositesb.2016.09.013.
- [14] M. Grigore, "Methods of Recycling, Properties and Applications of Recycled Thermoplastic Polymers," *Recycling*, vol. 2, no. 4, p. 24, Nov. 2017, doi: 10.3390/recycling2040024.
- [15] P. Treenate, "'CLEANER PRODUCTION FOR ACHIEVING SUSTAINABLE DEVELOPMENT GOALS' Life Cycle Management for Plastic Waste Management: A Life Cycle Assessment of Polyethylene Bag in Thailand."
- [16] C. L. Simões, L. M. C. Pinto, and C. A. Bernardo, "Environmental and economic analysis of end of life management options for an HDPE product using a life cycle thinking approach," *Waste Management and Research*, vol. 32, no. 5, pp. 414–422, 2014, doi: 10.1177/0734242X14527334.
- [17] A. Ruban and G. L. Gallardo Fernandez, "Examensarbete i Hållbar Utveckling 74 Life Cycle Assessment of Plastic Bag Production Life Cycle Assessment of Plastic Bag Production Anna Ruban."
- [18] K. Ragaert, L. Delva, and K. van Geem, "Mechanical and chemical recycling of solid plastic waste," *Waste Management*, vol. 69. Elsevier Ltd, pp. 24–58, Nov. 01, 2017. doi: 10.1016/j.wasman.2017.07.044.
- [19] J. N. Díaz de León *et al.*, "Noble metals supported on binary γ -Al₂O₃- α -Ga₂O₃ oxide as potential low-temperature water-gas shift catalysts," *Fuel*, vol. 266, Apr. 2020, doi: 10.1016/J.FUEL.2020.117031.
- [20] H. P. Wang and K. S. Lin, "Gasification of waste gases," *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, vol. 32, no. 7, pp. 1989–1997, 1997, doi: 10.1080/10934529709376661.
- [21] J.G. Speigh, "Cogasification - an overview | ScienceDirect Topics," 2015.
- [22] S. Farzad, M. A. Mandegari, and J. F. Görgens, "A critical review on biomass gasification, co-gasification, and their environmental assessments," *Biofuel*

- Research Journal*, vol. 3, no. 4. Green Wave Publishing of Canada, pp. 483–495, Dec. 01, 2016. doi: 10.18331/BRJ2016.3.4.3.
- [23] N. Couto, A. Rouboa, V. Silva, E. Monteiro, and K. Bouziane, “Influence of the biomass gasification processes on the final composition of syngas,” in *Energy Procedia*, Jan. 2013, vol. 36, pp. 596–606. doi: 10.1016/j.egypro.2013.07.068.
 - [24] H. Tian, J. Li, M. Yan, Y. W. Tong, C. H. Wang, and X. Wang, “Organic waste to biohydrogen: A critical review from technological development and environmental impact analysis perspective,” *Applied Energy*, vol. 256, p. 113961, Dec. 2019, doi: 10.1016/J.APENERGY.2019.113961.
 - [25] G. Lopez, M. Artetxe, M. Amutio, J. Alvarez, J. Bilbao, and M. Olazar, “Recent advances in the gasification of waste plastics. A critical overview,” *Renewable and Sustainable Energy Reviews*, vol. 82. Elsevier Ltd, pp. 576–596, Feb. 01, 2018. doi: 10.1016/j.rser.2017.09.032.
 - [26] S. Czernik and R. J. French, “Production of hydrogen from plastics by pyrolysis and catalytic steam reform,” *Energy and Fuels*, vol. 20, no. 2, pp. 754–758, Mar. 2006, doi: 10.1021/ef050354h.
 - [27] I. Barbarias *et al.*, “Pyrolysis and in-line catalytic steam reforming of polystyrene through a two-step reaction system,” *Journal of Analytical and Applied Pyrolysis*, vol. 122, pp. 502–510, Nov. 2016, doi: 10.1016/j.jaap.2016.10.006.
 - [28] C. Wu and P. T. Williams, “A novel Ni-Mg-Al-CaO catalyst with the dual functions of catalysis and CO₂ sorption for H₂ production from the pyrolysis-gasification of polypropylene,” *Fuel*, vol. 89, no. 7, pp. 1435–1441, Jul. 2010, doi: 10.1016/j.fuel.2009.10.020.
 - [29] Y. Park, T. Namioka, S. Sakamoto, T. J. Min, S. A. Roh, and K. Yoshikawa, “Optimum operating conditions for a two-stage gasification process fueled by polypropylene by means of continuous reactor over ruthenium catalyst,” in *Fuel Processing Technology*, Aug. 2010, vol. 91, no. 8, pp. 951–957. doi: 10.1016/j.fuproc.2009.10.014.
 - [30] I. Barbarias *et al.*, “A sequential process for hydrogen production based on continuous HDPE fast pyrolysis and in-line steam reforming,” *Chemical Engineering Journal*, vol. 296, pp. 191–198, Jul. 2016, doi: 10.1016/j.cej.2016.03.091.
 - [31] T. Namioka *et al.*, “Hydrogen-rich gas production from waste plastics by pyrolysis and low-temperature steam reforming over a ruthenium catalyst,” *Applied Energy*, vol. 88, no. 6, pp. 2019–2026, Jun. 2011, doi: 10.1016/j.apenergy.2010.12.053.

- [32] I. Barbarias *et al.*, “Pyrolysis and in-line catalytic steam reforming of polystyrene through a two-step reaction system,” *Journal of Analytical and Applied Pyrolysis*, vol. 122, pp. 502–510, Nov. 2016, doi: 10.1016/j.jaap.2016.10.006.
- [33] T. Y. A. Fahmy, Y. Fahmy, F. Mobarak, M. El-Sakhawy, and R. E. Abou-Zeid, “Biomass pyrolysis: past, present, and future,” *Environment, Development and Sustainability*, vol. 22, no. 1. Springer, pp. 17–32, Jan. 01, 2020. doi: 10.1007/s10668-018-0200-5.
- [34] H. Al-Haj Ibrahim, “Introductory Chapter: Pyrolysis,” in *Recent Advances in Pyrolysis*, IntechOpen, 2020. doi: 10.5772/intechopen.90366.
- [35] C. Z. Zaman *et al.*, “Pyrolysis: A Sustainable Way to Generate Energy from Waste,” in *Pyrolysis*, InTech, 2017. doi: 10.5772/intechopen.69036.
- [36] L. Liu, M. Du, G. Li, J. Fan, and Y. Cai, “Pyrolysis Behavior and Product Distribution of Exinite Submacerals,” *Journal of Analytical and Applied Pyrolysis*, p. 104957, Oct. 2020, doi: 10.1016/j.jaap.2020.104957.
- [37] S. J. Kern, C. Pfeifer, and H. Hofbauer, “Cogasification of polyethylene and lignite in a dual fluidized bed gasifier,” *Industrial and Engineering Chemistry Research*, vol. 52, no. 11, pp. 4360–4371, Mar. 2013, doi: 10.1021/ie303453e.
- [38] L. Zaccariello and M. Mastellone, “Fluidized-Bed Gasification of Plastic Waste, Wood, and Their Blends with Coal,” *Energies (Basel)*, vol. 8, no. 8, pp. 8052–8068, Aug. 2015, doi: 10.3390/en8088052.
- [39] J. Gil, J. Corella, M. P. Aznar, and M. A. Caballero, “Biomass gasification in atmospheric and bubbling fluidized bed: Effect of the type of gasifying agent on the product distribution,” *Biomass and Bioenergy*, vol. 17, no. 5, pp. 389–403, Nov. 1999, doi: 10.1016/S0961-9534(99)00055-0.
- [40] R. Xiao, B. Jin, H. Zhou, Z. Zhong, and M. Zhang, “Air gasification of polypropylene plastic waste in fluidized bed gasifier,” *Energy Conversion and Management*, vol. 48, no. 3, pp. 778–786, Mar. 2007, doi: 10.1016/j.enconman.2006.09.004.
- [41] A. Erkiaga, G. Lopez, M. Amutio, J. Bilbao, and M. Olazar, “Syngas from steam gasification of polyethylene in a conical spouted bed reactor,” *Fuel*, vol. 109, pp. 461–469, Jul. 2013, doi: 10.1016/j.fuel.2013.03.022.
- [42] V. Dieterich, A. Buttler, A. Hanel, H. Spliethoff, and S. Fendt, “Power-to-liquid via synthesis of methanol, DME or Fischer–Tropsch-fuels: a review ,” *Energy &*

- Environmental Science*, vol. 13, no. 10, pp. 3207–3252, Oct. 2020, doi: 10.1039/d0ee01187h.
- [43] A. Masudi, N. W. Che Jusoh, and O. Muraza, “Recent progress on low rank coal conversion to dimethyl ether as clean fuel: A critical review,” *Journal of Cleaner Production*, vol. 277. Elsevier Ltd, p. 124024, Dec. 20, 2020. doi: 10.1016/j.jclepro.2020.124024.
 - [44] B. Prabowo, M. Yan, M. Syamsiro, R. H. Setyobudi, and M. K. Biddinika, “State of the Art of Global Dimethyl Ether Production and It’s Potential Application in Indonesia.”
 - [45] M. Andersen, K. A. Saetre, S. Fredriksen, and C. Pfeiffer, “Simulation of the Pyrolysis Process: from Plastic Waste to Environmental Friendly Fuel”, doi: 10.3384/ecp18153303.
 - [46] M. Syamsiro *et al.*, “Fuel Oil Production from Municipal Plastic Wastes in Sequential Pyrolysis and Catalytic Reforming Reactors,” *Energy Procedia*, vol. 47, pp. 180–188, 2014, doi: 10.1016/j.egypro.2014.01.212.
 - [47] Z. Yao, S. Yu, W. Su, W. Wu, J. Tang, and W. Qi, “Kinetic studies on the pyrolysis of plastic waste using a combination of model-fitting and model-free methods,” *Waste Management and Research*, vol. 38, no. 1_suppl, pp. 77–85, May 2020, doi: 10.1177/0734242X19897814.
 - [48] C. Cleetus, S. Thomas, and S. Varghese, “Synthesis of Petroleum-Based Fuel from Waste Plastics and Performance Analysis in a CI Engine,” *Journal of Energy*, vol. 2013, pp. 1–10, 2013, doi: 10.1155/2013/608797.
 - [49] A. Vijayakumar and J. Sebastian, “Pyrolysis process to produce fuel from different types of plastic - A review,” in *IOP Conference Series: Materials Science and Engineering*, Aug. 2018, vol. 396, no. 1. doi: 10.1088/1757-899X/396/1/012062.
 - [50] N. Deng, D. Li, Q. Zhang, A. Zhang, R. Cai, and B. Zhang, “Simulation analysis of municipal solid waste pyrolysis and gasification based on Aspen plus,” *Frontiers in Energy*, vol. 13, no. 1, pp. 64–70, Mar. 2019, doi: 10.1007/s11708-017-0481-7.
 - [51] P. Kannan, A. Al, and C. Srinivasak, “Optimization of Waste Plastics Gasification Process Using Aspen-Plus,” in *Gasification for Practical Applications*, InTech, 2012. doi: 10.5772/48754.
 - [52] C. A. Pereira, P. M. Coelho, J. F. Fernandes, and M. H. Gomes, “Study of an energy mix for the production of hydrogen,” *International Journal of Hydrogen*

- Energy*, vol. 42, no. 2, pp. 1375–1382, Jan. 2017, doi: 10.1016/J.IJHYDENE.2016.07.182.
- [53] J. M. Sánchez, M. M. Barreiro, and M. Maroño, “Bench-scale study of separation of hydrogen from gasification gases using a palladium-based membrane reactor,” *Fuel*, vol. 116, pp. 894–903, Jan. 2014, doi: 10.1016/J.FUEL.2013.02.051.
 - [54] T. da Silva Veras, T. S. Mozer, D. da Costa Rubim Messeder dos Santos, and A. da Silva César, “Hydrogen: Trends, production and characterization of the main process worldwide,” *International Journal of Hydrogen Energy*, vol. 42, no. 4, pp. 2018–2033, Jan. 2017, doi: 10.1016/J.IJHYDENE.2016.08.219.
 - [55] F. Dalena, A. Senatore, A. Marino, A. Gordano, M. Basile, and A. Basile, “Methanol Production and Applications: An Overview,” *Methanol: Science and Engineering*, pp. 3–28, Jan. 2018, doi: 10.1016/B978-0-444-63903-5.00001-7.
 - [56] A. Yuda, A. Ashok, and A. Kumar, “A comprehensive and critical review on recent progress in anode catalyst for methanol oxidation reaction,” <https://doi.org/10.1080/01614940.2020.1802811>, 2020, doi: 10.1080/01614940.2020.1802811.
 - [57] B. Balopi, P. Agachi, and Danha, “Methanol Synthesis Chemistry and Process Engineering Aspects- A Review with Consequence to Botswana Chemical Industries,” *Procedia Manufacturing*, vol. 35, pp. 367–376, Jan. 2019, doi: 10.1016/J.PROMFG.2019.05.054.
 - [58] A. Fivga and I. Dimitriou, “Pyrolysis of plastic waste for production of heavy fuel substitute: A techno-economic assessment,” *Energy*, vol. 149, pp. 865–874, Apr. 2018, doi: 10.1016/j.energy.2018.02.094.
 - [59] N. Emad and B. Vahid, “Hydrogen production from co-gasification of asphaltene and plastic,” *Petroleum Science and Technology*, vol. 37, no. 16, pp. 1905–1909, Aug. 2019, doi: 10.1080/10916466.2018.1458116.
 - [60] A. AlNouss, G. McKay, and T. Al-Ansari, “Enhancing waste to hydrogen production through biomass feedstock blending: A techno-economic-environmental evaluation,” *Applied Energy*, vol. 266, May 2020, doi: 10.1016/j.apenergy.2020.114885.
 - [61] T. Namioka *et al.*, “Hydrogen-rich gas production from waste plastics by pyrolysis and low-temperature steam reforming over a ruthenium catalyst,” *Applied Energy*, vol. 88, no. 6, pp. 2019–2026, Jun. 2011, doi: 10.1016/J.APENERGY.2010.12.053.

- [62] Y. Chai, N. Gao, M. Wang, and C. Wu, "H₂ production from co-pyrolysis/gasification of waste plastics and biomass under novel catalyst Ni-CaO-C," *Chemical Engineering Journal*, vol. 382, p. 122947, Feb. 2020, doi: 10.1016/J.CEJ.2019.122947.
- [63] J. C. Acomb, M. A. Nahil, and P. T. Williams, "Thermal processing of plastics from waste electrical and electronic equipment for hydrogen production," *Journal of Analytical and Applied Pyrolysis*, vol. 103, pp. 320–327, Sep. 2013, doi: 10.1016/J.JAAP.2012.09.014.
- [64] C. Wu and P. T. Williams, "Pyrolysis–gasification of plastics, mixed plastics and real-world plastic waste with and without Ni–Mg–Al catalyst," *Fuel*, vol. 89, no. 10, pp. 3022–3032, Oct. 2010, doi: 10.1016/J.FUEL.2010.05.032.
- [65] T. Namioka *et al.*, "Hydrogen-rich gas production from waste plastics by pyrolysis and low-temperature steam reforming over a ruthenium catalyst," *Applied Energy*, vol. 88, no. 6, pp. 2019–2026, Jun. 2011, doi: 10.1016/J.APENERGY.2010.12.053.
- [66] Y. Takafumi Kawamora, "Development of chemical recycle technology to methanol by partial oxidation of waste plastics," 2002. Accessed: Nov. 08, 2021. [Online]. Available: https://www.researchgate.net/publication/296434033_Development_of_chemical_recycle_technology_to_methanol_by_partial_oxidation_of_waste_plastics
- [67] U. Ahmed *et al.*, "Co-Production of Hydrogen and Methanol Using Fuel Mix Systems: Technical and Economic Assessment," *Applied Sciences* 2021, Vol. 11, Page 6577, vol. 11, no. 14, p. 6577, Jul. 2021, doi: 10.3390/APP11146577.
- [68] U. Ahmed, "Techno-economic analysis of dual methanol and hydrogen production using energy mix systems with CO₂ capture," *Energy Conversion and Management*, vol. 228, p. 113663, Jan. 2021, doi: 10.1016/J.ENCONMAN.2020.113663.
- [69] J. Loipersböck, M. Luisser, S. Müller, H. Hofbauer, and R. Rauch, "Experimental Demonstration and Validation of Hydrogen Production Based on Gasification of Lignocellulosic Feedstock," *ChemEngineering* 2018, Vol. 2, Page 61, vol. 2, no. 4, p. 61, Dec. 2018, doi: 10.3390/CHEMENGINEERING2040061.
- [70] T. Li, T. Shoinkhorova, J. Gascon, and J. Ruiz-Martinez, "Aromatics Production via Methanol-Mediated Transformation Routes," *ACS Catalysis*, vol. 11, no. 13, pp. 7780–7819, Jul. 2021, doi: 10.1021/ACSCATAL.1C01422.

- [71] E. Jakab, G. Várhegyi, and O. Faix, “Thermal decomposition of polypropylene in the presence of wood-derived materials,” *Journal of Analytical and Applied Pyrolysis*, vol. 56, no. 2, pp. 273–285, Nov. 2000, doi: 10.1016/S0165-2370(00)00101-7.
- [72] G. Lopez, A. Erkiaga, M. Amutio, J. Bilbao, and M. Olazar, “Effect of polyethylene co-feeding in the steam gasification of biomass in a conical spouted bed reactor,” *Fuel*, vol. 153, pp. 393–401, Mar. 2015, doi: 10.1016/j.fuel.2015.03.006.
- [73] V. Wilk and H. Hofbauer, “Co-gasification of plastics and biomass in a dual fluidized-bed steam gasifier: Possible interactions of fuels,” *Energy and Fuels*, vol. 27, no. 6, pp. 3261–3273, Jun. 2013, doi: 10.1021/ef400349k.
- [74] I. I. Ahmed, N. Nipattummakul, and A. K. Gupta, “Characteristics of syngas from co-gasification of polyethylene and woodchips,” *Applied Energy*, vol. 88, no. 1, pp. 165–174, Jan. 2011, doi: 10.1016/j.apenergy.2010.07.007.
- [75] F. Pinto, C. Franco, R. N. André, M. Miranda, I. Gulyurtlu, and I. Cabrita, “Co-gasification study of biomass mixed with plastic wastes,” *Fuel*, vol. 81, no. 3, pp. 291–297, Feb. 2002, doi: 10.1016/S0016-2361(01)00164-8.
- [76] P. Kannan, A. Al, and C. Srinivasak, “Optimization of Waste Plastics Gasification Process Using Aspen-Plus,” in *Gasification for Practical Applications*, InTech, 2012. doi: 10.5772/48754.
- [77] D. Saebea, P. Ruengrit, A. Arpornwichanop, and Y. Patcharavorachot, “Gasification of plastic waste for synthesis gas production,” in *Energy Reports*, Feb. 2020, vol. 6, pp. 202–207. doi: 10.1016/j.egyr.2019.08.043.
- [78] A. Fivga and I. Dimitriou, “Pyrolysis of plastic waste for production of heavy fuel substitute: A techno-economic assessment,” *Energy*, vol. 149, pp. 865–874, Apr. 2018, doi: 10.1016/j.energy.2018.02.094.
- [79] A. Vijayakumar and J. Sebastian, “Pyrolysis process to produce fuel from different types of plastic - A review,” in *IOP Conference Series: Materials Science and Engineering*, Aug. 2018, vol. 396, no. 1, p. 012062. doi: 10.1088/1757-899X/396/1/012062.
- [80] J. Udomsirichakorn and P. A. Salam, “Review of hydrogen-enriched gas production from steam gasification of biomass: The prospect of CaO-based chemical looping gasification,” *Renewable and Sustainable Energy Reviews*, vol. 30. Pergamon, pp. 565–579, Feb. 01, 2014. doi: 10.1016/j.rser.2013.10.013.

- [81] P. Ebrahimi, A. Kumar, and M. Khraisheh, "A review of recent advances in water-gas shift catalysis for hydrogen production," *Emergent Materials*, vol. 3, no. 6. Springer Nature, pp. 881–917, Dec. 01, 2020. doi: 10.1007/s42247-020-00116-y.
- [82] A. Qayyum, U. Ali, and N. Ramzan, "Acid gas removal techniques for syngas, natural gas, and biogas clean up—a review," *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. Taylor and Francis Inc., 2020. doi: 10.1080/15567036.2020.1800866.
- [83] H. Jahangiri, J. Bennett, P. Mahjoubi, K. Wilson, and S. Gu, "A review of advanced catalyst development for Fischer-Tropsch synthesis of hydrocarbons from biomass derived syn-gas," *Catalysis Science and Technology*, vol. 4, no. 8. Royal Society of Chemistry, pp. 2210–2229, Jul. 07, 2014. doi: 10.1039/c4cy00327f.
- [84] "Aspen Plus ® Aspen Plus User Guide," 1981, Accessed: Oct. 11, 2021. [Online]. Available: <http://www.aspentech.com>
- [85] Q. Zhang, L. Dor, L. Zhang, W. Yang, and W. Blasiak, "Performance analysis of municipal solid waste gasification with steam in a Plasma Gasification Melting reactor," *Applied Energy*, vol. 98, pp. 219–229, Oct. 2012, doi: 10.1016/J.APENERGY.2012.03.028.
- [86] I. N. Zaini, A. Nurdiawati, and M. Aziz, "Cogeneration of power and H₂ by steam gasification and syngas chemical looping of macroalgae," *Applied Energy*, vol. 207, pp. 134–145, Dec. 2017, doi: 10.1016/J.APENERGY.2017.06.071.
- [87] J. Jin *et al.*, "A solar methane reforming reactor design with enhanced efficiency," *Applied Energy*, vol. 226, pp. 797–807, Sep. 2018, doi: 10.1016/J.APENERGY.2018.04.098.
- [88] M. N. Khan and T. Shamim, "Investigation of hydrogen generation in a three reactor chemical looping reforming process," *Applied Energy*, vol. 162, pp. 1186–1194, Jan. 2016, doi: 10.1016/J.APENERGY.2015.08.033.
- [89] N. Ahmad, N. Ahmad, and U. Ahmed, "Process design and techno-economic evaluation for the production of platform chemical for hydrocarbon fuels from lignocellulosic biomass using biomass-derived γ -valerolactone," *Renewable Energy*, vol. 161, pp. 750–755, Dec. 2020, doi: 10.1016/J.RENENE.2020.07.028.
- [90] X. Chen, F. Xi, Y. Geng, and T. Fujita, "The potential environmental gains from recycling waste plastics: Simulation of transferring recycling and recovery technologies to Shenyang, China," *Waste Management*, vol. 31, no. 1, pp. 168–179, Jan. 2011, doi: 10.1016/J.WASMAN.2010.08.010.

- [91] D. Saebea, P. Ruengrit, A. Arpornwichanop, and Y. Patcharavorachot, "Gasification of plastic waste for synthesis gas production," *Energy Reports*, vol. 6, pp. 202–207, 2020, doi: 10.1016/j.egyr.2019.08.043.
- [92] S. Likhittaphon *et al.*, "Effect of CuO/ZnO catalyst preparation condition on alcohol-assisted methanol synthesis from carbon dioxide and hydrogen," *International Journal of Hydrogen Energy*, pp. 20782–20791, Aug. 2019, doi: 10.1016/j.ijhydene.2018.07.021.
- [93] U. Hamid, A. Rauf, U. Ahmed, M. Selim Arif Sher Shah, and N. Ahmad, "Techno-economic assessment of process integration models for boosting hydrogen production potential from coal and natural gas feedstocks," *Fuel*, vol. 266, Apr. 2020, doi: 10.1016/j.fuel.2020.117111.
- [94] M. W. Seo *et al.*, "Methanol absorption characteristics for the removal of H₂S (hydrogen sulfide), COS (carbonyl sulfide) and CO₂ (carbon dioxide) in a pilot-scale biomass-to-liquid process," *Energy*, vol. 66, pp. 56–62, Mar. 2014, doi: 10.1016/j.energy.2013.08.038.
- [95] U. Ahmed, "Techno-economic analysis of dual methanol and hydrogen production using energy mix systems with CO₂ capture," *Energy Conversion and Management*, vol. 228, Jan. 2021, doi: 10.1016/j.enconman.2020.113663.
- [96] J. P. Lange, "Methanol synthesis: a short review of technology improvements," *Catalysis Today*, vol. 64, no. 1–2, pp. 3–8, Jan. 2001, doi: 10.1016/S0920-5861(00)00503-4.
- [97] F. Nestler *et al.*, "Kinetic modelling of methanol synthesis over commercial catalysts: A critical assessment," *Chemical Engineering Journal*, vol. 394, p. 124881, Aug. 2020, doi: 10.1016/J.CEJ.2020.124881.
- [98] G. H. Graaf, + H Scholtens, E. J. Stamhuis, and A. A. C. M. Beenackers, "INTRA-PARTICLE DIFFUSION LIMITATIONS IN LOW-PRESSURE METHANOL SYNTHESIS," 1990.
- [99] S. C. Mccaul, "Simulation and Techno-Economic Analysis of the AChT Green Methanol Process," 2019.
- [100] G. H. Graaf, P. J. J. M. Sijtsema, E. J. Stamhuist, and G. E. H. Joostes, "CHEMICAL EQUILIBRIA IN METHANOL SYNTHESIS," 1986.
- [101] S. Werner, "Ultra-low Temperature Water-gas Shift Reaction with Supported Ionic Liquid Phase (SILP) Catalysts: Wassergas-Shift-Katalyse Mit Geträgern

Ionischen Flüssigkeiten Unter Extrem Mil.” [Online]. Available: www.crt.cbi.uni-erlangen.de

- [102] P. Kannan, A. Al Shoaibi, and C. Srinivasakannan, “Process simulation and sensitivity analysis of waste plastics gasification in a fluidized bed reactor”, doi: 10.2495/WM120171.
- [103] N. Al Amoodi, P. Kannan, A. Al Shoaibi, and C. Srinivasakannan, “ASPEN PLUS SIMULATION OF POLYETHYLENE GASIFICATION UNDER EQUILIBRIUM CONDITIONS,” *Chemical Engineering Communications*, vol. 200, no. 7, pp. 977–992, Jul. 2013, doi: 10.1080/00986445.2012.715108.
- [104] N. Al Amoodi, P. Kannan, A. Al Shoaibi, and C. Srinivasakannan, “Chemical Engineering Communications ASPEN PLUS SIMULATION OF POLYETHYLENE GASIFICATION UNDER EQUILIBRIUM CONDITIONS,” *Chemical Engineering Communications*, no. 7, pp. 977–992, 2013, doi: 10.1080/00986445.2012.715108.
- [105] P. Kannan, A. Al Shoaibi, and C. Srinivasakannan, “Energy recovery from co-gasification of waste polyethylene and polyethylene terephthalate blends,” *Computers and Fluids*, vol. 88, pp. 38–42, 2013, doi: 10.1016/j.compfluid.2013.09.004.
- [106] P. Kannan, G. Lakshmanan, A. Al Shoaibi, and C. Srinivasakannan, “Equilibrium model analysis of waste plastics gasification using CO₂ and steam,” *Waste Management and Research*, vol. 35, no. 12, pp. 1247–1253, Dec. 2017, doi: 10.1177/0734242X17736946.
- [107] P. Kannan, A. Al, and C. Srinivasak, “Optimization of Waste Plastics Gasification Process Using Aspen-Plus,” in *Gasification for Practical Applications*, InTech, 2012. doi: 10.5772/48754.
- [108] P. Ranjan, P. Kannan, A. Al Shoaibi, and C. Srinivasakannan, “Modeling of Ethane Thermal Cracking Kinetics in a Pyrocracker,” *Chemical Engineering & Technology*, vol. 35, no. 6, p. n/a-n/a, May 2012, doi: 10.1002/ceat.201100529.
- [109] F. Olofsson and H. Halvarsson, “SMALL SCALE ENERGY CONVERSION,” 2020.
- [110] C. Wu and P. T. Williams, “Hydrogen production by steam gasification of polypropylene with various nickel catalysts,” *Applied Catalysis B: Environmental*, vol. 87, no. 3–4, pp. 152–161, 2009, doi: 10.1016/j.apcatb.2008.09.003.

- [111] R. Xiao, B. Jin, H. Zhou, Z. Zhong, and M. Zhang, "Air gasification of polypropylene plastic waste in fluidized bed gasifier," *Energy Conversion and Management*, vol. 48, no. 3, pp. 778–786, 2007, doi: 10.1016/j.enconman.2006.09.004.
- [112] M. He, B. Xiao, Z. Hu, S. Liu, X. Guo, and S. Luo, "Syngas production from catalytic gasification of waste polyethylene: Influence of temperature on gas yield and composition," *International Journal of Hydrogen Energy*, vol. 34, no. 3, pp. 1342–1348, 2009, doi: 10.1016/j.ijhydene.2008.12.023.
- [113] A. Erkiaga, G. Lopez, M. Amutio, J. Bilbao, and M. Olazar, "Syngas from steam gasification of polyethylene in a conical spouted bed reactor," *Fuel*, vol. 109, pp. 461–469, 2013, doi: 10.1016/j.fuel.2013.03.022.
- [114] G. Editors *et al.*, "Kinetic Based Simulation of Methane Steam Reforming and Water Gas Shift for Hydrogen Production Using Aspen Plus," in *CHEMICAL ENGINEERING TRANSACTIONS*, 2017, vol. 56. doi: 10.3303/CET1756281.
- [115] Y. F. Wang, C. H. Tsai, W. Y. Chang, and Y. M. Kuo, "Methane steam reforming for producing hydrogen in an atmospheric-pressure microwave plasma reactor," *International Journal of Hydrogen Energy*, vol. 35, no. 1, pp. 135–140, Jan. 2010, doi: 10.1016/j.ijhydene.2009.10.088.
- [116] K. Großmann, P. Treiber, and J. Karl, "Steam methane reforming at low S/C ratios for power-to-gas applications," *International Journal of Hydrogen Energy*, vol. 41, no. 40, pp. 17784–17792, Oct. 2016, doi: 10.1016/j.ijhydene.2016.08.007.
- [117] S. A. Ghoneim, R. A. El-Salamony, and S. A. El-Temtamy, "Review on Innovative Catalytic Reforming of Natural Gas to Syngas," *World Journal of Engineering and Technology*, vol. 04, no. 01, pp. 116–139, 2016, doi: 10.4236/wjet.2016.41011.
- [118] S. S. Khalafalla, U. Zahid, A. G. Abdul Jameel, U. Ahmed, F. S. Alenazey, and C. J. Lee, "Conceptual design development of coal-to-methanol process with carbon capture and utilization," *Energies (Basel)*, vol. 13, no. 23, Dec. 2020, doi: 10.3390/en13236421.
- [119] U. Ahmed *et al.*, "Co-production of hydrogen and methanol using fuel mix systems: Technical and economic assessment," *Applied Sciences (Switzerland)*, vol. 11, no. 14, Jul. 2021, doi: 10.3390/app11146577.
- [120] U. Ahmed, U. Zahid, and C. Han, "IGCC Modelling for Simultaneous Power Generation and CO₂ Capture," *Computer Aided Chemical Engineering*, vol. 37, pp. 2381–2386, 2015, doi: 10.1016/B978-0-444-63576-1.50091-1.

- [121] U. Zahid, F. N. al Rowaili, M. K. Ayodeji, and U. Ahmed, "Simulation and parametric analysis of CO₂ capture from natural gas using diglycolamine," *International Journal of Greenhouse Gas Control*, vol. 57, pp. 42–51, Feb. 2017, doi: 10.1016/J.IJGGC.2016.12.016.
- [122] U. Ahmed, U. Zahid, Y. S. Jeong, C. J. Lee, and C. Han, "IGCC process intensification for simultaneous power generation and CO₂ capture," *Chemical Engineering and Processing: Process Intensification*, vol. 101, pp. 72–86, Mar. 2016, doi: 10.1016/J.CEP.2015.12.012.
- [123] Q. Zhu, *High temperature syngas coolers*. 2015.
- [124] G. H. Graaf, E. J. Stamhuis, and A. A. C. M. Beenackersz, "KINETICS OF LOW-PRESSURE METHANOL SYNTHESIS," 1988.
- [125] J. F. Portha *et al.*, "Kinetics of Methanol Synthesis from Carbon Dioxide Hydrogenation over Copper-Zinc Oxide Catalysts," *Industrial and Engineering Chemistry Research*, vol. 56, no. 45, pp. 13133–13145, Nov. 2017, doi: 10.1021/acs.iecr.7b01323.
- [126] C. H. Bartholomew and R. J. Farrauto, "Fundamentals of Industrial Catalytic Processes: Second Edition," *Fundamentals of Industrial Catalytic Processes: Second Edition*, pp. 1–966, Aug. 2010, doi: 10.1002/9780471730071.
- [127] H. H. Kung, "DEACTIVATION OF METHANOL SYNTHESIS CATALYSTS-A REVIEW," 1992.
- [128] R. Timsina *et al.*, "EasyChair Preprint Methanol Synthesis from Syngas: a Process Simulation Methanol synthesis from syngas: a process simulation," 2021.
- [129] Sofiane ARAB, "Développement d'un procédé de synthèse de méthanol à partir de CO₂ et H₂," 2014. Accessed: Nov. 11, 2021. [Online]. Available: <https://hal.univ-lorraine.fr/tel-01751246/document>
- [130] I. L. Motta, N. T. Miranda, R. Maciel Filho, and M. R. Wolf Maciel, "Biomass gasification in fluidized beds: A review of biomass moisture content and operating pressure effects," *Renewable and Sustainable Energy Reviews*, vol. 94. Elsevier Ltd, pp. 998–1023, Oct. 01, 2018. doi: 10.1016/j.rser.2018.06.042.
- [131] M. Hafiz Kamarudin *et al.*, "A review on different forms and types of waste plastic used in concrete structure for improvement of mechanical properties," *Journal of Advanced Research in Applied Mechanics Journal homepage*, vol. 28, pp. 9–30, 2016, [Online]. Available: www.akademiabaru.com/aram.html

- [132] N. R. Mitta, S. Ferrer-Nadal, A. M. Lazovic, J. F. Parales, E. Velo, and L. Puigjaner, “Modelling and simulation of a tyre gasification plant for synthesis gas production,” *Computer Aided Chemical Engineering*, vol. 21, no. C, pp. 1771–1776, Jan. 2006, doi: 10.1016/S1570-7946(06)80304-4.
- [133] Y. S. Jeong, K. B. Park, and J. S. Kim, “Hydrogen production from steam gasification of polyethylene using a two-stage gasifier and active carbon,” *Applied Energy*, vol. 262, p. 114495, Mar. 2020, doi: 10.1016/J.APENERGY.2020.114495.
- [134] R. Xiao, B. Jin, H. Zhou, Z. Zhong, and M. Zhang, “Air gasification of polypropylene plastic waste in fluidized bed gasifier,” *Energy Conversion and Management*, vol. 48, no. 3, pp. 778–786, Mar. 2007, doi: 10.1016/J.ENCONMAN.2006.09.004.
- [135] D. J. Harris, D. G. Roberts, and D. G. Henderson, “Gasification behaviour of Australian coals at high temperature and pressure,” *Fuel*, vol. 85, no. 2, pp. 134–142, Jan. 2006, doi: 10.1016/J.FUEL.2005.07.022.
- [136] M. Baláš, M. L. Lis’y, and O. O. Otaštelcl, “The Effect of Temperature on the Gasification Process,” vol. 52, no. 4, 2012.
- [137] D. E. Garrett, “Chemical Engineering Economics,” *Chemical Engineering Economics*, 1989, doi: 10.1007/978-94-011-6544-0.
- [138] “Elements of Chemical Reaction Engineering Fifth Edition.”
- [139] “Hydrogen Basics - Production.”
<http://www.fsec.ucf.edu/en/consumer/hydrogen/basics/production.htm> (accessed Oct. 11, 2021).
- [140] “Linde, Hydrogen Utopia to deploy plastic waste-to-hydrogen technology in Poland | S&P Global Platts.” <https://www.spglobal.com/platts/en/market-insights/latest-news/electric-power/090621-linde-hydrogen-utopia-to-deploy-plastic-waste-to-hydrogen-technology-in-poland> (accessed Oct. 11, 2021).
- [141] N. Technical Contact and M. Ruth, “Hydrogen Production Cost Estimate Using Biomass Gasification: Independent Review,” 2010, doi: 10.13140/RG.2.2.10346.57280.
- [142] “Economic analysis of biomass gasification for generating electricity in rural areas in Indonesia”, doi: 10.1088/1757-899X/334/1/012012.

- [143] J. Nyári, M. Magdeldin, M. Larimi, M. Järvinen, and A. Santasalo-Aarnio, “Techno-economic barriers of an industrial-scale methanol CCU-plant,” *Journal of CO2 Utilization*, vol. 39, p. 101166, Jul. 2020, doi: 10.1016/J.JCOU.2020.101166.
- [144] U. Ahmed, “Techno-economic feasibility of methanol synthesis using dual fuel system in a parallel process design configuration with control on green house gas emissions,” *International Journal of Hydrogen Energy*, vol. 45, no. 11, pp. 6278–6290, Feb. 2020, doi: 10.1016/j.ijhydene.2019.12.169.
- [145] F. di Gregorio, *Fuel Gas Technology for Biomass and Waste Environmental and Techno-Economic Assessments*, no. June. 2012. [Online]. Available: <http://www.amracenter.com/doc/pubblicazioni/DiGregorio-PhD-thesis.pdf>
- [146] X. Chen, F. Xi, Y. Geng, and T. Fujita, “The potential environmental gains from recycling waste plastics: Simulation of transferring recycling and recovery technologies to Shenyang, China,” *Waste Management*, vol. 31, no. 1, pp. 168–179, Jan. 2011, doi: 10.1016/j.wasman.2010.08.010.
- [147] R. Miandad *et al.*, “Catalytic pyrolysis of plastic waste: Moving toward pyrolysis based biorefineries,” *Frontiers in Energy Research*, vol. 7, no. MAR, 2019, doi: 10.3389/fenrg.2019.00027.
- [148] M. H. Morten W. Ryberg, Alexis Laurent, “Mapping of global plastics value chain and plastics losses to the environment (with a particular focus on marine environment),” 2018. Accessed: Oct. 31, 2020. [Online]. Available: [https://gefmarineplastics.org/files/2018 Mapping of global plastics value chain and hotspots - final version r181023.pdf](https://gefmarineplastics.org/files/2018%20Mapping%20of%20global%20plastics%20value%20chain%20and%20hotspots%20-%20final%20version%20r181023.pdf)
- [149] S. Erdogan, “Recycling of Waste Plastics into Pyrolytic Fuels and Their Use in IC Engines,” in *Sustainable Mobility*, IntechOpen, 2020. doi: 10.5772/intechopen.90639.
- [150] Q. Hu, Z. Tang, D. Yao, H. Yang, J. Shao, and H. Chen, “Thermal behavior, kinetics and gas evolution characteristics for the co-pyrolysis of real-world plastic and tyre wastes,” *Journal of Cleaner Production*, vol. 260, p. 121102, Jul. 2020, doi: 10.1016/j.jclepro.2020.121102.
- [151] Y. B. Sonawane, M. R. Shindikar, and M. Y. Khaladkar, “Calorific value,” vol. 16, pp. 879–882, 2017, Accessed: Oct. 31, 2020. [Online]. Available: www.neptjournal.com
- [152] M. Labaki and M. Jeguirim, “Thermochemical conversion of waste tyres—a review,” *Environmental Science and Pollution Research*, vol. 24, no. 11, pp. 9962–9992, Apr. 2017, doi: 10.1007/s11356-016-7780-0.

- [153] B. Shen, C. Wu, R. Wang, B. Guo, and C. Liang, "Pyrolysis of scrap tyres with zeolite USY," *Journal of Hazardous Materials*, vol. 137, no. 2, pp. 1065–1073, 2006, doi: 10.1016/j.jhazmat.2006.03.040.
- [154] A. Mohajerani *et al.*, "Recycling waste rubber tyres in construction materials and associated environmental considerations: A review," *Resources, Conservation and Recycling*, vol. 155. Elsevier B.V., p. 104679, Apr. 01, 2020. doi: 10.1016/j.resconrec.2020.104679.

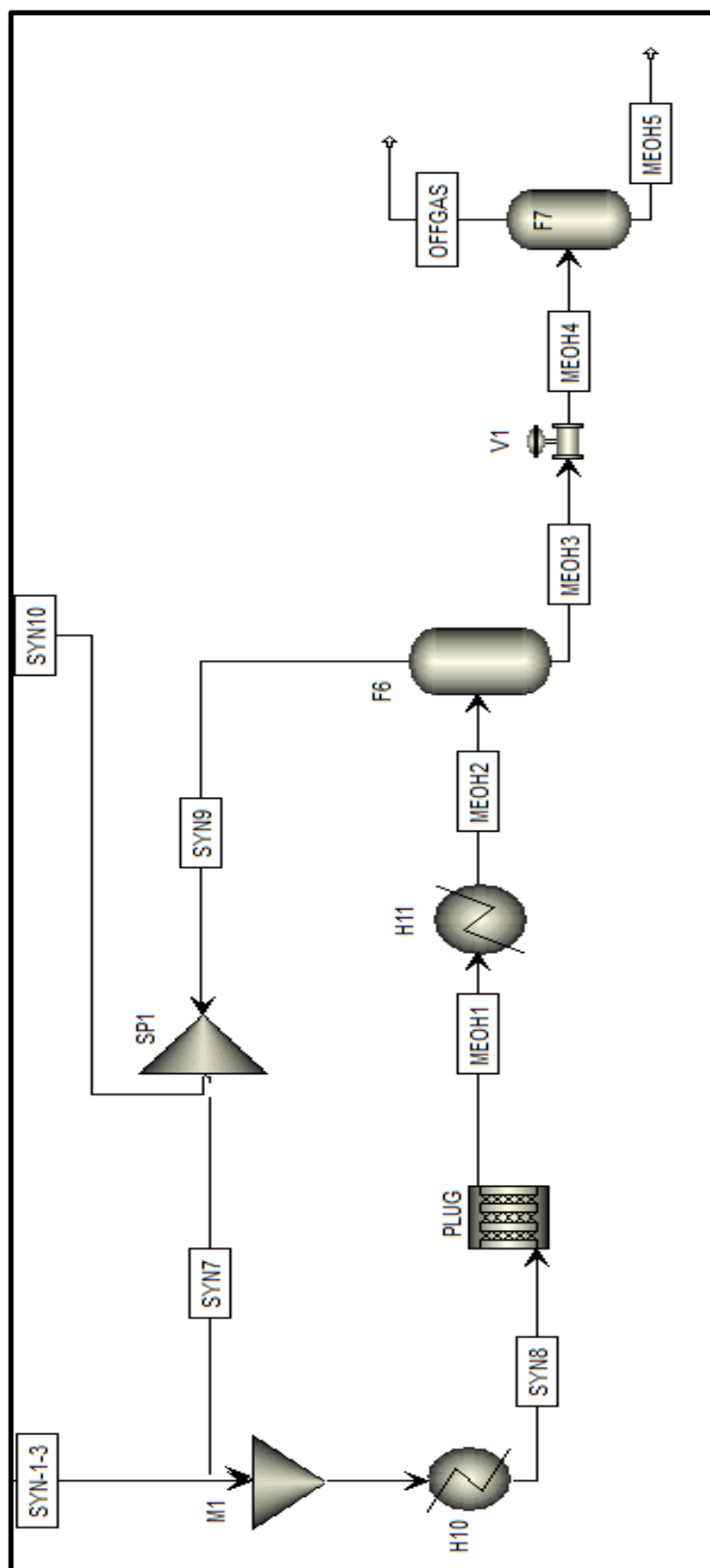


Figure 41 Methanol synthesis unit in case 3 (base case design)

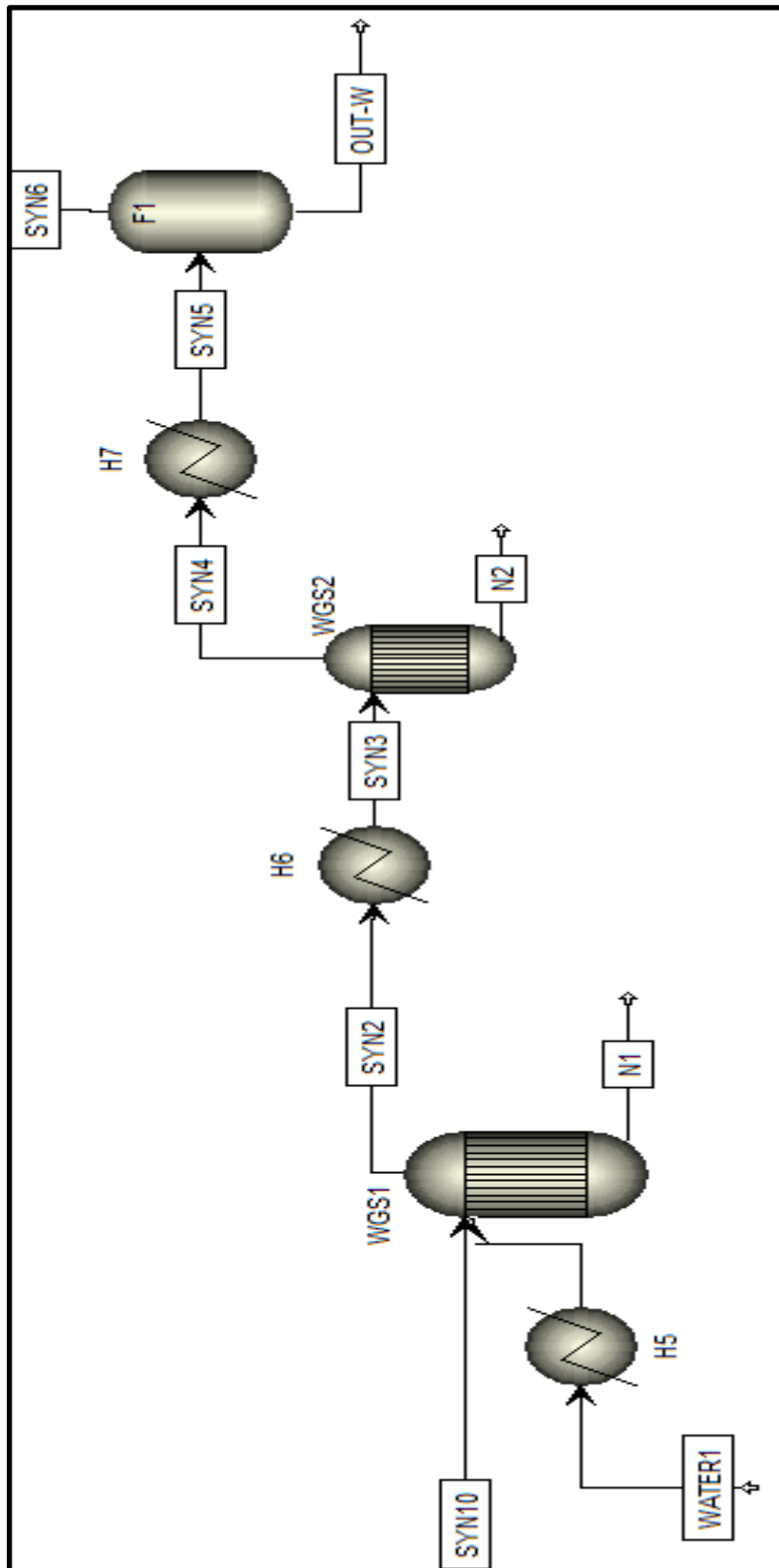


Figure 42 WGS unit in case 3 (base case design)

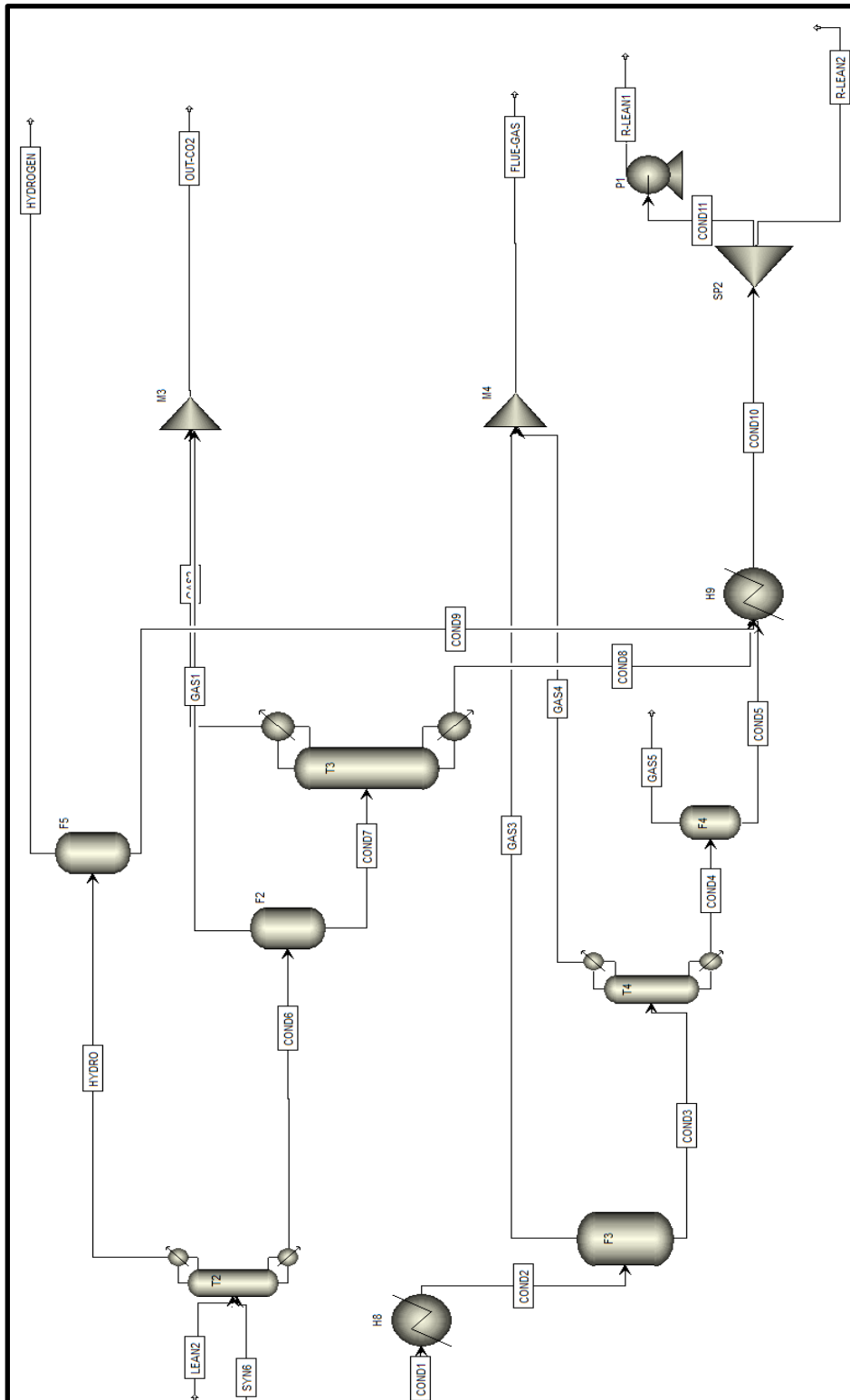


Figure 43 CO₂ removal unit with the solvent regeneration in case 3 (base case design)

A2. The Alternative Case for Dual Hydrogen and Methanol production (Case 4)

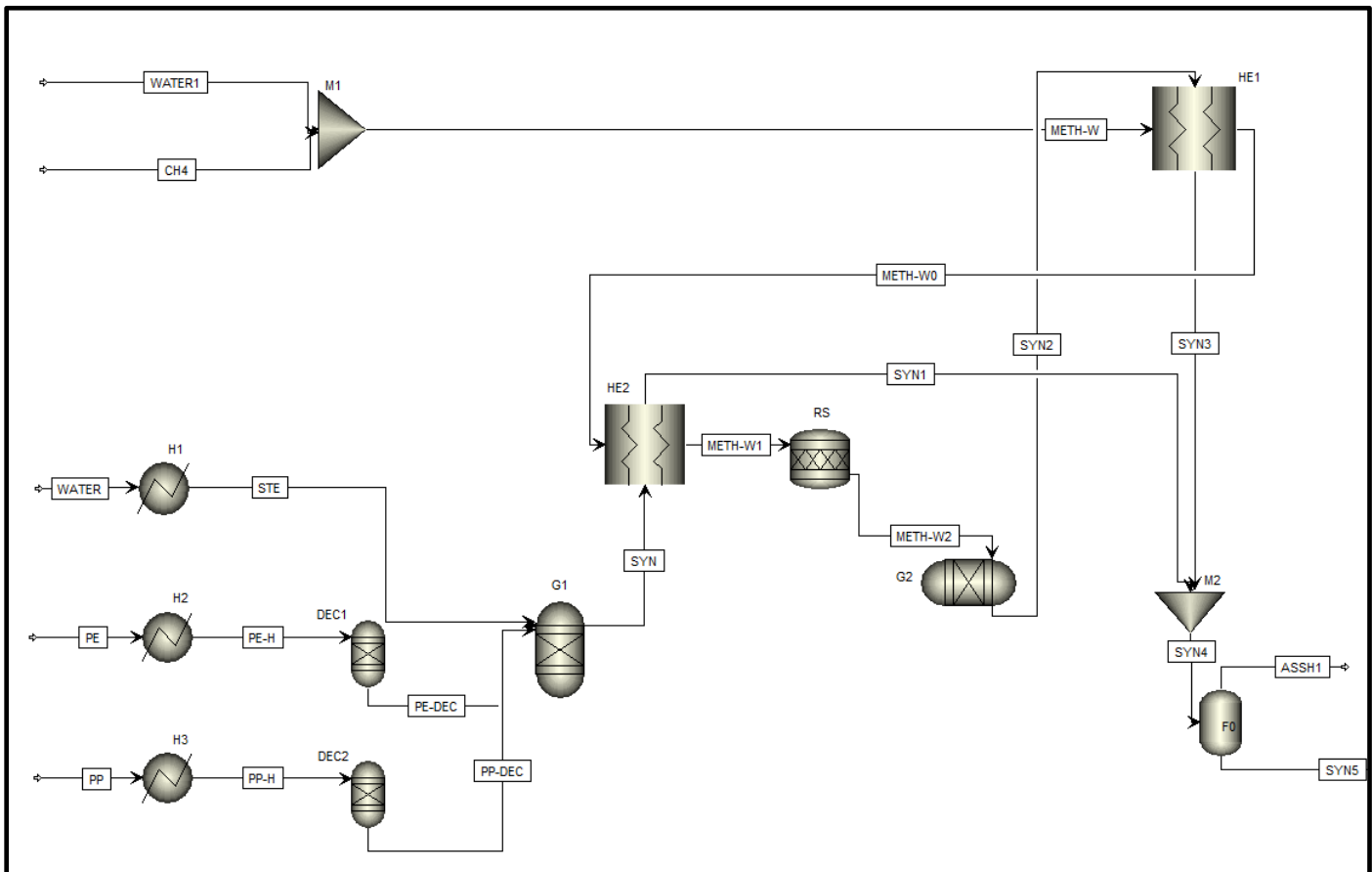


Figure 44 Steam gasification and SMR units in case 4 (the alternative case)

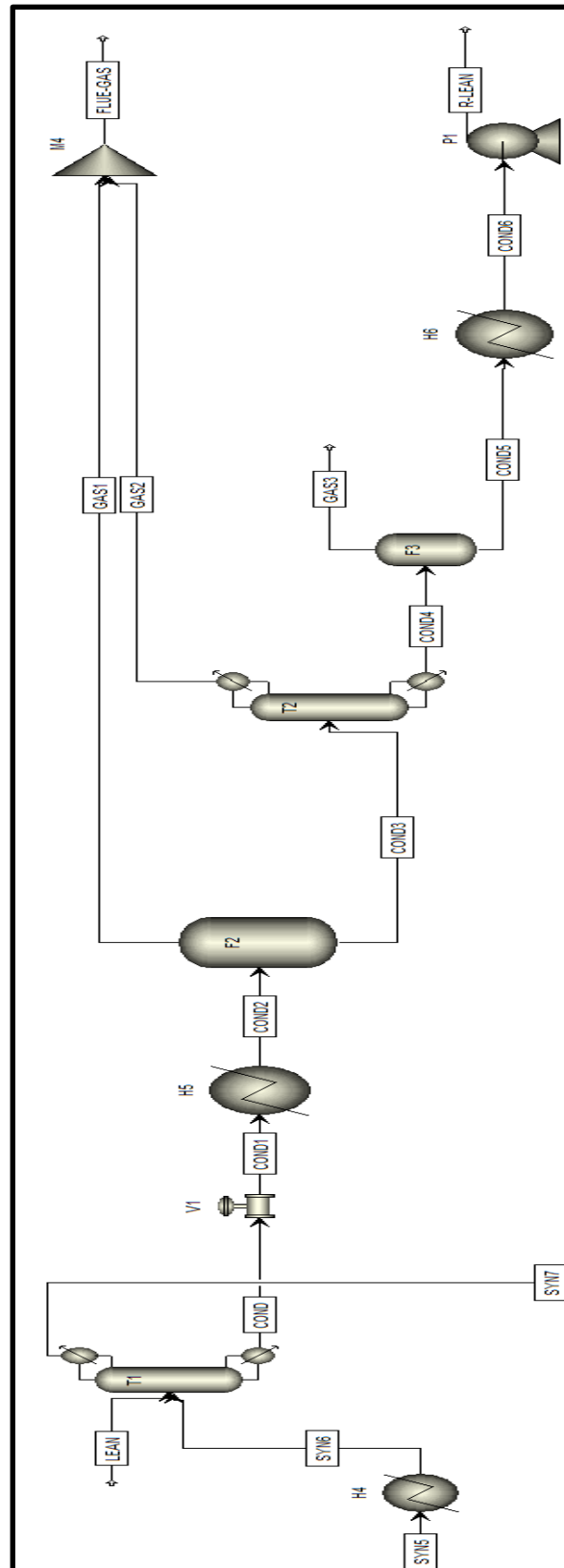


Figure 45 H₂S removal with the solvent regeneration in case 4 (the alternative case)

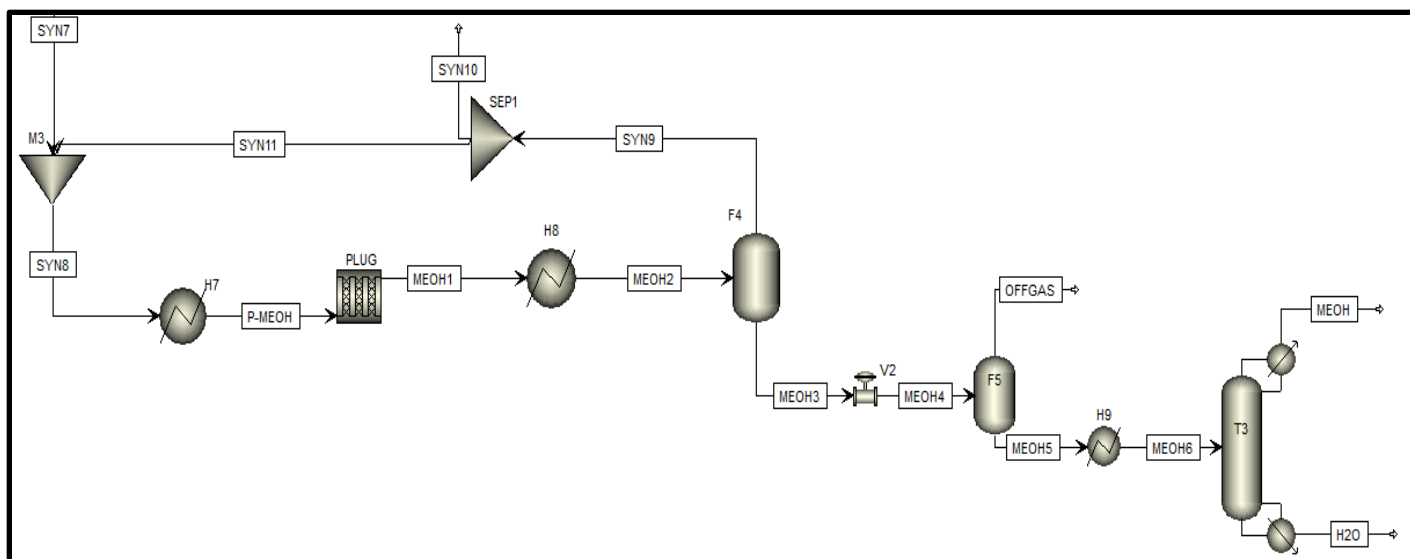


Figure 46 Methanol synthesis unit in case 4 (the alternative case)

Appendix B: Kinetics Keyed to the ASPEN Interphase

Table 24 Kinetic factors and driving forces parameters inputted to the ASPEN interphase

Kinetic Factor Reaction 1		Driving Force Reaction 1		
k (A)	1056.24		Term1	Term2
E (-B)	66200	A	0	29.06
n	0	B	0	-11833
Kinetic Factor Reaction 2		Driving Force Reaction 2		
k (A)	0.076		Term1	Term2
E (-B)	25800	A	0	24.39
n	0	B	0	-7059.73
Kinetic Factor Reaction 3		Driving Force Reaction 3		
k (A)	679620		Term1	Term2
E (-B)	91200	A	0	-4.67
n	0	B	0	4773.259

Table 25 Adsorption constants inputted to the ASPEN interphase

Adsorption Term						
Term no.	1	2	3	4	5	6
Coefficient A	0	-10.74	-14.17	-18.87	-29.61	-33.04
Coefficient B	0	5629.06	7421.22	10103.44	15732.50	17524.66
Coefficient C	0	0	0	0	0	0
Coefficient D	0	0	0	0	0	0

1) CO + 2 H₂ --> METHA-01(MIXED)

Reacting phase **Vapor** Rate basis **Cat (wt)**

LHHW kinetic expression

$$r = \frac{[\text{Kinetic factor}][\text{Driving force expression}]}{[\text{Adsorption expression}]}$$

Kinetic factor

If To is specified Kinetic factor = $k(T/T_o)^n e^{-(E/R)[1/T-1/T_o]}$

If To is not specified Kinetic factor = $kT^n e^{-E/RT}$

k **1060**

n **0**

E **66200** **kJ/kmol**

To **C**

Solids

Driving Force

Adsorption

Figure 47 The kinetic factor for CO hydrogenation to methanol

☒ Driving Force Expression

Reacting phase: Vapor

[Ci] basis: Partial pressure

Enter term: Term 1

Term 1

Concentration exponents for reactants		Concentration exponents for products	
Component	Exponent	Component	Exponent
CO	1	METHA-01	0
H2	1.5		

Coefficients for driving force constant

A: 0 B: 0 C: 0 D: 0

Figure 48 The CO hydrogenation driving force plugged to Aspen interphase for the first term

☒ Driving Force Expression

Reacting phase: Vapor

[Ci] basis: Partial pressure

Enter term: Term 2

Term 2

Concentration exponents for reactants		Concentration exponents for products	
Component	Exponent	Component	Exponent
CO	0	METHA-01	1
H2	-0.5		

Coefficients for driving force constant

A: 29.06 B: -11833 C: 0 D: 0

Figure 49 The CO hydrogenation driving force plugged to Aspen interphase for the second term

2) CO₂ + 3 H₂ --> METHA-01(MIXED) + H₂O(MIXED)

Reacting phase: **Vapor** Rate basis: **Cat (wt)**

LHHW kinetic expression

$$r = \frac{[\text{Kinetic factor}][\text{Driving force expression}]}{[\text{Adsorption expression}]}$$

Kinetic factor

If To is specified Kinetic factor = $k(T/T_o)^n e^{-(E/R)[1/T-1/T_o]}$

If To is not specified Kinetic factor = $kT^n e^{-E/RT}$

k: **0.0768**

n: **0**

E: **25800** **kJ/kmol**

To: **C**

Solids

Driving Force

Adsorption

Figure 50 The kinetic factor for CO₂ hydrogenation to methanol

☒ Driving Force Expression

Reacting phase: **Vapor**

[C_i] basis: **Partial pressure**

Enter term: **Term 1**

Term 1

Concentration exponents for reactants		Concentration exponents for products			
	Component	Exponent			
▶	CO ₂	1	▶	METHA-01	0
▶	H ₂	1.5	▶	H ₂ O	0

Coefficients for driving force constant

A: **0** B: **0** C: **0** D: **0**

Figure 51 The CO₂ hydrogenation driving force plugged to Aspen interphase for the first term

☒ Driving Force Expression

Reacting phase: Vapor

[Ci] basis: Partial pressure

Enter term: Term 2

Term 2

Concentration exponents for reactants		Concentration exponents for products	
	Component	Exponent	
▶	CO2	0	▶
▶	H2	-1.5	▶
			▶
			METHA-01
			1
			H2O
			1

Coefficients for driving force constant

A: 24.39 B: -7059.73 C: 0 D: 0

Figure 52 The CO₂ hydrogenation driving force plugged to Aspen interphase for the second term

3) CO2 + H2 --> CO(MIXED) + H2O(MIXED)

Reacting phase: Vapor Rate basis: Cat (wt)

LHHW kinetic expression

$$r = \frac{[\text{Kinetic factor}][\text{Driving force expression}]}{[\text{Adsorption expression}]}$$

Kinetic factor

If To is specified Kinetic factor = $k(T/T_o)^n e^{-(E/R)[1/T-1/T_o]}$

If To is not specified Kinetic factor = $kT^n e^{-E/RT}$

k: 680000

n: 0

E: 91200 kJ/kmol

To: C

Solids

Driving Force

Adsorption

Figure 53 The kinetic factor for the RWGS reaction

☒ Driving Force Expression

Reacting phase: Vapor

[Ci] basis: Partial pressure

Enter term: Term 1

Term 1

Concentration exponents for reactants		Concentration exponents for products	
Component	Exponent	Component	Exponent
CO2	1	CO	0
H2	1	H2O	0

Coefficients for driving force constant

A: 0 B: 0 C: 0 D: 0

Figure 54 The RWGS reaction driving force plugged to Aspen interphase for the first term

☒ Driving Force Expression

Reacting phase: Vapor

[Ci] basis: Partial pressure

Enter term: Term 2

Term 2

Concentration exponents for reactants		Concentration exponents for products	
Component	Exponent	Component	Exponent
CO2	0	CO	1
H2	0	H2O	1

Coefficients for driving force constant

A: -4.67 B: 4773.26 C: 0 D: 0

Figure 55 The RWGS reaction driving force plugged to Aspen interphase for the second term

☒ **Adsorption Expression**

Reacting phase:

[Ci] basis:

Adsorption expression exponent:

Concentration exponents

	Component	Term no. 1	Term no. 2	Term no. 3	Term no. 4	Term no. 5	Term no. 6
▶	H2	0.5	0.5	0.5	0	0	0
▶	CO	0	1	0	0	1	0
▶	CO2	0	0	1	0	0	1
▶	H2O	0	0	0	1	1	1

Adsorption constants

	Term no.	1	2	3	4	5	6
▶	Coefficient A	0	-10.7	-14.2	-18.9	-29.6	-33
▶	Coefficient B	0	5629.06	7421.22	10103.4	15732.5	17524.7
▶	Coefficient C	0	0	0	0	0	0
▶	Coefficient D	0	0	0	0	0	0

Figure 56 ASPEN Plus interphase for the input of Graaf.et.al kinetics to synthesize methanol using PFR reactor (adsorption expression)

Vitae

Name	:Ali Abdullah Al-Qadri
Nationality	:Yemen
Date of Birth	:3/4/1994
Email	:alialqadriabdullah96@gmail.com
Address	:IBB/ Al-HAZM
Academic Background	:BS at KFUPM in Chemical Engineering with a Minor in Math Awarded in 2019 MS at KFUPM in Chemical Engineering to be Awarded in 2022

Submitted Papers

- **Polymers MDPI:** Techno-economic Feasibility of Hydrogen Production from Waste Plastics
- **International Journal of Hydrogen Energy:** Techno-economic Analysis of Dual Hydrogen and Methanol Production from Plastics Using Energy Integrated System