



UNIVERSITAT DE  
BARCELONA



ALMA MATER STUDIORUM  
UNIVERSITÀ DI BOLOGNA



UNIVERSIDADE DO ALGARVE

**COAL FUEL GAS CLEANING BY NON-THERMAL PULSED CORONA  
DISCHARGE PLASMA AND “REACH” REGULATION  
COMPATIBILITY ASSESSEMENT FOR TRACE ELEMENTS  
EXTRACTION FROM GASIFICATION ASH**

**Bazarsad Narmandakh**

Dissertation

**Erasmus Mundus Master in Chemical Innovation and Regulation**

Work supervised by

**Prof. Isabel Cavaco**

**Dr. Nicolas Spiegl**

Air Liquide Global E&C Solutions Germany GmbH

**2016**



**TABLE OF CONTENT:**

ABSTRACT: .....	4
ACRONYMS.....	5
TABLES AND FIGURES.....	7
1. INTRODUCTION.....	9
2. METHODOLOGY.....	11
3. CONTEXT.....	13
3.1. COAL.....	13
3.2. COAL GASIFICATION.....	15
3.2.1. Gasifier types.....	15
3.2.2. Coal Syngas Composition.....	18
3.2.3. Coal Syngas applications.....	21
3.2.4. Syngas quality requirements.....	24
3.3. SYNGAS CLEANING METHOD AND TECHNOLOGIES.....	25
3.3.1. PARTICULATE MATTER REMOVAL.....	26
3.3.2. SULPHUR COMPOUND REMOVAL.....	27
3.3.3. NITROGEN COMPOUND REMOVAL.....	27
3.3.4. TAR REMOVAL.....	28
4. GAS CLEANING TECHNOLOGY SELECTION.....	40
4.1. CASES.....	40
4.1.1. SMALL CASE.....	41
4.1.2. LARGE CASE.....	41
4.2. PULSED CORONA DISCHARGE PLASMA SIMULATION RESULTS:.....	44
4.2.1. SMALL CASE-1500 kg/hr (daf) COAL AS FEED.....	44
4.2.2. LARGE CASE-26400 kg/hr (daf) COAL AS FEED.....	46
4.2.3. ENERGY CONSUMPTION FOR PLASMA REACTOR.....	47
4.3. APPLICATION MATCHING.....	48
4.3.1. AMMONIA PRODUCTION.....	48
4.3.2. FUEL GAS.....	49
4.4. SENSITIVITY ANALYSIS.....	50
4.5. MARKET RESEARCH.....	53
4.5.1. CURRENT-STATE-OF-ART.....	53
4.5.2. FEASIBILITY OF FIXED-BED GASIFIER & PLASMA.....	54
4.6. ECONOMIC COMPETITIVES OF PLASMA IN FUEL GAS APPLCATION.....	59
4.7. PROCESS FLOW DIAGRAM.....	67
4.8. PATENT SEARCH FOR COAL FUEL GAS CLEANING BY PLASMA UNIT.....	68
5. COAL GASIFICATION ASH HANDLING.....	70
5.1. REVIEW ON COAL COMBUSTION/GASIFICATION ASHES.....	70
5.2. FEASIBILITY OF TRACE ELEMENT EXTRACTION FROM CCPs.....	73
5.2.1. TRACE ELEMENTS IN RAW COAL.....	75
5.2.2. PARTITIONING FATE OF TRACE ELEMENTS IN FIXED-BED GASIFIER.....	79
5.2.3. QUANTIFICATION OF TRACE ELEMENTS IN COAL ASH.....	84
5.3. COAL COMBUSTION/GASIFICATION ASH REGULATION.....	85
5.3.1. WASTE DIRECTIVE.....	85
5.3.2. REACH REGULATION.....	87
5.4. SUMMARY.....	90
6. CONCLUSION.....	93
REFERENCES.....	95
APPENDICES.....	99

### ABSTRACT:

Atmospheric small-scaled fixed-bed gasifiers fed with cheap low rank sub-bituminous coal produces syngas (CO and H<sub>2</sub>) with high tar content, which is one of the impurities produced along the main syngas from coal gasifications. This organic impurity with high molecular weight hydrocarbons is of interest as they polymerize or condense to more complex structures throughout the involved process pipers or heat exchangers, leading to fouling and attrition problems, which eventually leads to lose of overall plant efficiency and increased operation costs. To avoid such event, either expensive non-tar forming coal (semi-Anthracite or Anthracite) must be used or an effective tar removal unit integration in the overall process should be made.

Plasma is the fourth state of matter and it contains free radical, ions and excited molecules and they create a highly reactive atmosphere as these reactive species carry enough energy to initiate tar decomposition reactions. Non-thermal plasmas are already successfully utilized in air pollution control for the VOC removal. Within the non-thermal pulsed corona discharge plasma scope, Technical university of Eindhoven (TU/e) studied biomass tar reforming (naphthalene as the tar model) and various syngas compositions were tested to study their impact on tar removal process. Furthermore, non-thermal pulsed corona discharge plasma is found to be effective in tar reforming and is created by supplying electricity and nitrogen gas to the plasma reactor. Created plasma dissociates the CO<sub>2</sub> components in the syngas into CO and O radicals, which the unstable reactive O radicals oxidize tars into light hydrocarbons (CH<sub>4</sub>). 50% nitrogen content in the syngas due to plasma requirement limits its usage only as fuel gas for heating or electricity generation.

After determining utilizing of plasma together with atmospheric fixed-bed gasifier is technologically possible, the demand for it in fuel gas application to generate heat is researched. The research involved carefully looking at energy policy of that chosen particular country and their main source of energies. According to the International Energy Agency's 2015 statistics, China and India are placed largest coal consumers in the non-OECD countries ranking. It was estimated that China currently needs over 8000 fixed-bed gasifier (8000 plasmas) to meet the industrial heat demand. Assuming a similar development in India, in total 2000 fixed-bed-gasifiers will be needed in the next years. In the researched countries, current alternative method to generate heat instead of Natural gas or LPG is fuel gas via coal gasification. Non-tar forming quality coal are gasified, but they are either expensive due to the high demand and are not widely available. Syngas from this case is cleaned through electrostatic precipitator light tar collectors (if present) before utilizing it. These fuel gas-cleaning methods are to remove very small amount of light tars (if present) and dusts. It is a common practice in developing countries to produce fuel gas via coal gasification for the purpose of heat and electricity generation. It was found that this method is cost effective than using natural gas or LPG. Furthermore, it was found that fuel gas generation via plasma-involved case were even more cost effective than the current state of art case by at least 10%. The fuel gas production cost via plasma involved proposing configuration is competitive over the fuel gas production cost from the current state of art. In addition to cost benefits, plasma cleaned fuel gas production approach allows utilizing of low rank coal and does not utilize water, hence fresh water consumption and pollution is prevented.

Abundantly available coal ashes are potential untapped resource for trace elements (TE). In 2014, the European union member states (EU-28) had consumed 285 million tones of hard coal and based on the world trace elements average in world coal, the available TE for extraction exceeds 1 tonne per year. Therefore, TE extraction from available coal ashes in EU-28 is subject to REACH regulation. However, there is no entry on ECHA database for such process. The entries at ECHA database regarding coal ash are only for the utilization for construction materials purpose. Lack of commercially available extraction technology optimized for coal ash, limited understanding of trace elements modes of occurrence, origin, and toxicological data relating to all possible chemical contaminants rising from extraction process are not well understood and are not presently available. More research and development effort must be done in order to obtain these missing information and to perform full chemical characterization of the coal ash to optimize trace elements extraction process for that particular coal and to identify all possible waste streams. Such that, needed toxicological data according to REACH regulation is obtained.

### ACRONYMS

- ASU – Air Separation Units
- B.C-Boundary Conditions
- BS-Boiler slag
- CCPs-Coal Combustion products
- CGPs-Coal Gasification products
- CHP-Combined Heat Power
- COS- Carbonyl Sulfide
- CTC – Coal to Chemicals
- CTL – Coal to Liquids
- CTO – Coal to Olefins
- CV-Calorific value
- DAF coal -Dry Ash Free Coal
- DBI – Deutsches Brennstoffinstitut
- DCL – Direct Conversion Process for Coal to Liquids
- DC-Corona discharges
- DEA-Diethanol Amine
- BFD-Block flow diagram
- DME – Coal to Dimethylether
- ECHA-European Chemical Agency
- ECOBA- European Coal Combustion Products Association
- ECN- The Energy research Centre of the Netherlands
- EPA-Environmental Protection Agency
- EU-European Union
- ESP- Electrostatic precipitator
- FA-Fly ash
- FBDB – Fixed Bed, Dry Bottom Gasifier
- FBC-Fluidized Bed Combustion
- FGD- Flue Gas Desulphurisation
- FOB-Free On Board
- FT- Fischer Tropsch
- FTIR- Fourier transform infrared spectroscopy
- GC-Gas chromatography
- GDP-Gross domestic product
- GE – General Electric Corporation
- GHG- Green House Gas
- HAP- Hazardous Air Pollutants
- HTW- High temperature Winkler
- HCN-Hydrogen Cyanide
- HEHC-High Electricity and High Coal Price
- HELC- High Electricity and Low Coal
- ID – Internal Diameter
- IEA- International Energy Agency
- ICE- Internal gas engine
- JFE-Japanese Engineering Corporation
- LEHC-Low Electricity and High Coal price
- LELC-Low Electricity and Low Coal
- LNG – Liquefied Natural Gas
- LHV- Low heating value
- LPG- Liquefied Petroleum Gas
- LO-CAT process- Hydrogen Sulfide removal technology
- MK<sup>+</sup> - MK Plus<sup>TM</sup> – Advanced Lurgi Fixed Bed Dry Bottom Gasifier
- MTG-Methanol to Gasoline
- MEA-Mono Ethanol Amine
- NG-Natural Gas
- OLGA- Dutch Oil based gas cleaning technology
- ORS- Oil recovery system

- OECD- Organization for Economic Co-operation and Development
- PRC – People’s Republic of China
- Pre-SIEF- Pre Substance Information Exchange Forum
- R and D – Research and Development
- REACH-Registration, Evaluation, Authority of Chemicals
- REE-Rare Earth Elements
- RE- Relative Enrichment Factor
- RF plasma-Radio Frequency plasma
- ROI – Return on Investment
- SDA-Spray Dry Absorption
- SFG – Siemens Fuel Entrained Flow Gasifier
- SIF- Substance Identity Profile
- SPC – State Power Corporation Commission of China
- SNG-Synthetic Natural Gas (coal based natural gas)
- TPD – Tonnes per Day
- Tdaf-Tonnes per dry ash free coal
- TU/e- Technical University of Eindhoven, The Netherlands
- USD – United States Dollar
- US-DOE-U.S. Department of Energy
- VOC-Volatile Organic Compound
- WGS –Water Gas Shift reaction
- WWCCPN- World Wide Coal Combustion Product Network

**TABLES AND FIGURES**

Table 1: Toxic pollutants from coal burning/gasification and associated health problems .....	14
Table 2: Differences between conventional coal combustion and modern gasification processes .....	15
Table 3: Summary of different types of coal gasifiers commercially available .....	17
Table 4: Effect of gasifier gasification agent on heating value of the produced syngas .....	19
Table 5: Table 4: Gas quality requirement for power generation .....	24
Table 6: Acceptance and preferable fuel gas specification for modern engines .....	24
Table 7: Summary of coal syngas impurities and available technologies to clean .....	25
Table 8: Biomass tar classification by ECN .....	28
Table 9: : Composition summary of catalysts .....	31
Table 10: Summary of nickel-based catalyst in syngas tar removal .....	32
Table 11: Summary of non-nickel based catalysts in syngas tar removal.....	33
Table 12: Pulsed corona discharge plasma utilization applications .....	37
Table 13: OLGA technology references.....	39
Table 14: Gasifier specification .....	41
Table 15: Feedstock (Coal and Coal) analysis result summary .....	42
Table 16: Tar yield from coal gasification .....	43
Table 17: Syngas generation simulation results for Coal and Tar and mixed.....	45
Table 18: Syngas generation simulation result for Coal and Tar and mixed.....	46
Table 19: Energy consumption of plasma unit.....	47
Table 20: Syngas exiting the plasma reactor .....	48
Table 21: Syngas exiting the plasma reactor .....	49
Table 22: Effect of carbon by-pass percentage increase on fuel gas composition .....	51
Table 23: Effect of increased oxygen radical termination by the hydrogen in the fuel gas .....	52
Table 24: Coal to Natural gas projects in China [89] .....	55
Table 25: Heat production and consumption by area in China .....	56
Table 26: Syngas specification exiting the plasma from small gasifier case .....	57
Table 27: Syngas specification exiting the plasma from small gasifier case .....	57
Table 28: Indian heat consumption estimation [91, 92] .....	58
Table 29: Proposals summary obtained through Alibaba site .....	59
Table 30: Cost break-down of proposal- .....	60
Table 31: Gas-engine quotation summary for plasma configuration obtained through Alibaba site....	60
Table 32: Output comparison (MW) of State-of-Art (Alibaba), Plasma configuration with and without Gas-Engine against the current sold price of Natural Gas and LPG in China.....	62
Table 33: Production cost comparison of different cases against market price of NG and LPG .....	63
Table 34: Economic analysis for plasma case with various prices for Electricity and Coal .....	64
Table 35: Economic analysis for plasma case with various prices for coal and gas engine (Yes/No)..	64
Table 36: Material balance for above shown overall simplified block flow diagram .....	67
Table 37: Patent search result for non-thermal pulsed corona discharge plasma.....	68
Table 38: The coal ash production in E-28 member states .....	71
Table 39: Commercial plants recovering alumina from coal ash in China .....	73
Table 40: Metal extraction from coal ash technology developer examples .....	74
Table 41: Common minerals in coal and their elemental compositions .....	76
Table 42: Traces elements mode of occurrence probability in coal .....	78
Table 43: Trace elements average values of China, South-Africa and global average [113-115] .....	79
Table 44: Trace elements quantifications .....	85
Table 45: Registration of CCPs (Status 30.07.2016) .....	90
Table 46: Fuel gas production cost through two options against current actual price of NG and LPG	93

Figure 1: Coal ranking .....	14
Figure 2: Fixed-bed gasifier .....	17
Figure 3: Fluidized bed gasifier .....	17
Figure 4: Entrained-flow-gasifier .....	18
Figure 5: Temperature gradient of fixed-bed gasifier.....	20
Figure 6: Variety of ways that syngas can be used .....	24
Figure 7: Brief summary of Hot gas particulate matter removal technologies .....	26
Figure 8: Efficiencies of particulate matter removal technologies with change in particle size ( $\mu\text{m}$ )	27
Figure 9: Tar reforming reaction mechanism in the presence of Hydrogen and Water .....	29
Figure 10: Naphthalene decomposition scheme .....	37
Figure 11: Experimental set up .....	37
Figure 12: Tar dew point control principle in OLGA technology .....	39
Figure 13: Working principles of OLGA technology.....	39
Figure 14: Coal analytical result reporting different basis .....	40
Figure 15: Structural chart of the ambient fixed- bed gasifier .....	42
Figure 16: High pressure fixed-bed gasifier .....	42
Figure 17: BFD of coal gasification with FBDB-gasifier with pulsed corona discharge plasma .....	45
Figure 18: Fuel gas application with Gas-Engine integrated.....	50
Figure 19: CHP system efficiency of GE .....	50
Figure 20: Fuel gas application with combined heat and power system .....	50
Figure 21: Current state-of-art configuration- .....	54
Figure 22: Residential gas consumption in China .....	54
Figure 23: Fuel gas pipelines in China .....	55
Figure 24: Current-State-of-Art configuration utilized in China to generate fuel gas for heating .....	61
Figure 25: Proposing plasma configuration with no gas-engine .....	61
Figure 26: Proposing plasma configuration with gas-engine integrated .....	62
Figure 27: LELC case comparison against the State-of-Art case with varying plasma cost-NG.....	65
Figure 28: LELC case comparison against the State-of-Art case with varying plasma cost-LPG.....	65
Figure 29: Overall block-flow diagram of ambient FBDB small scaled gasifier integrated with non-thermal pulsed corona plasma discharge reactor for fuel gas generation for heating application.....	68
Figure 30: CCPs production statistics by country in 2010 (million tonnes) .....	70
Figure 31: Utilization ash utilisation (%) by country in 2010 .....	71
Figure 32: Coal Combustion Products (CCPs) development in EU-15 from 1993 to 2012.....	72
Figure 33: Utilization and disposal rate of CCPs in EU-15 in 2010 .....	72
Figure 34: Trace element classification based on their volatility behavior .....	81
Figure 35: Reaction zones in Sasol_Lurgi fixed-bed-dry-bottom gasification process .....	81
Figure 36: Trace elements partitioning path summary in Fixed-bed type coal gasifier .....	84
Figure 37: Hard coal consumption in EU-28 between 1990-2014 (1990=100%) .....	85
Figure 38: Waste hierarchy in the EU Directive 2008/98/EC .....	86
Figure 39: REACH information requirements- Tests .....	90



### 1. INTRODUCTION

The Earth we live in is an environment system of living things and provides capacity for living space and to supply energy. Our survival on earth depends on limited resources, yet world population is increasing as if it were infinite. Our population is expected to reach 10 billion by the end of the century [1]. This is leading to lower natural resource consumption rate in order to reduce the impact we have on the planet and to preserve the health and beauty of the world we live in.

Coal is the world's most abundant organic fossil fuel. According to the International Energy Agency's coal information, the total proven reserves of the world are 1,000 billion tonnes and are spread over more than 70 countries across the globe [2]. Coal is recognized as a high priority component for many country's energy strategy. China peaked in coal consumption in 2013 and 50% of the total world's coal consumption were consumed solely by China in 2014 [3]. The most intensive coal growth world has ever experienced was due to China (fastest economic growth) and lead the world price of coal to its peak.

On 12<sup>th</sup> November 2014, China and USA, the world's two biggest economies and polluters reached agreement to cut their emissions. This was the first time that China agreed on carbon cuts and the first time for US to commit to deep reduction by 2025 [3]. This lead to a start of the world's coal boom to decline and world's price of coal to diminish. Because, China had accelerated its retreat from imported coal and this had huge implication on coal importing countries. This resulted China to have structural permanent changes of 1) Energy intensity growth and 2) Diversification of electricity supply away from coal. Moreover, China is undertaking everything they can to diversify their electricity supply as fast as they can. This can be seen from the fact that China had increase in electricity demand, yet reduced coal consumption in 2015. They use more power, but more power were from solar, wind, nuclear, gas and hydroelectricity.

While China is reducing its coal consumptions, there is an excess supply of coal that is not going to be converted. At the same time, there are some developing countries where coal demand continues to grow. For example, there are many people in India in remote areas living without supply of electricity and Indian energy sector is committed to ensure every citizen in India gets power by 2019[4]. As a result, India's coal consumption of their own cheap coal in coal powered power plants will continue to increase to the level that western countries had consumed 150 years ago. India intents to open up more coal mines in order to implement the target of supplying electricity. This is one of their actions to become less dependent on imported coal.

At the same time, renewable energy (solar, wind, nuclear) seems to be moving faster towards becoming reality. However, their full implementation to overtake any other energy source is limited due to its storage barrier and is being solved with help of technology advancement of battery storage system. There are several companies with their own solution of battery system with very affordable prices, this includes electric car company TESLA, which introduced its battery storage system and is taking parts in major biddings to deliver its batteries to the biggest electricity providers [5, 6].Development of such battery storage system to support renewable energy seems to be the game changer and renewable energy exploitation on the back of cheap storage system has the potential to revolutionize electricity generation and will be another bad news for coal's future. While researchers are working towards making the elusive promise of dependable renewable energy a reality, Coal is still a chosen source for energy, electricity, power generation in 2016 and coal's outlook within the next 10 years are still uncertain with the current innovation pace of renewable energies for the developing world.

Researchers in this field are researching in the hopes of developing efficient commercially available and affordable carbon capturing system in coal handling industries by 2050 [7]. This has resulted the world's very first carbon capturing system (>90%) and is integrated on brown coal fed SASK power plant in Canada in 2014 and it prevents 1 million tonnes of carbon dioxide (CO<sub>2</sub>) release yearly [8]. The project is worth \$1.4 billion and with this much investment, it is impossible to successfully implement the carbon capture throughout the globe and compete against renewable energy. However, not much improvement in cost reduction of carbon capture system has been seen over the last few years, while there are fast improvement in renewable energy technologies.

Coal energy dependent countries are utilizing commercially available gasification technologies to generate fuel gas to meet their energy demand. Fuel gases are composed of hydrocarbon (methane), hydrogen and carbon monoxide. Fuel gases are sources of heat energy that can be transmitted and distributed through pipes from the original source to the destination of the consumption. Resulted fuel gas from commercially large scaled gasification plants are cleaned from their unwanted impurities with help of available fuel cleaning technologies. However, these cleaning technologies are not suitable for small-scaled gasification plants due to technical and economical constraints. Conversion of coal for industrial combustion process through small-scaled gasification units is very common in countries, such as in China, India, Indonesia [9]. To avoid unwanted impurities in small-scaled gasification process, high rank coal is used, which is expensive and is not widely available. Moreover, current fuel gas cleaning technologies involve use of fresh water for cleaning which is not environmentally friendly. Therefore, there exists the need of new solution to clean the fuel gas from small scaled gasification unit, hence to improve the life the people by minimizing the pollutants released and reducing the amount of fresh water consumed. Thus, the first part this research work focuses on fuel gas cleaning technologies; particularly tar removal from the fuel gas and commercially available cleaning technologies will be looked closer for improvement or for suggesting new technology.

Furthermore, ash is a by-product of the gasification or combustion processes, which consists of bottom and fly ashes. The largest sources of world's coal ash are from coal-fired power and heat production plants. In 2010, it was estimated that in total 780 million tones of CCPs from energy sector were produced world wide, which on average 53% of them were utilized further for various applications. Coal is one of the main fuels in the energy sector of many countries. Utilization of coal for energy purpose results production of coal ash, commonly referred as CCPs (Coal Combustion Products). Coal ash disposal is a controversial topic as it is often debated that the coal ash from thermal processes contains traces of heavy metals sourcing from the raw coal. By definition, trace elements refers to chemical elements that are present in a natural material at concentrations <0.1% wt or 1000 µg/g. Abundantly available coal combustion ashes are potential untapped resource for trace elements that can alleviate supply shortage of transition elements. The future of technology advancement and sustainable and efficient energy generations are dependent on availability of trace elements. Therefore, the second part of this research focuses on REACH regulation compatibility assessment for trace elements extraction from gasification ash.

Energy is what sustains prosperity of the world and coal is the world's principal source of energy and will be for many decades to come. The finding from this research work will somehow be part of clean coal technology and will serve in improving the coal's outlook.

### 2. METHODOLOGY

The present work was performed in order to fulfill two objectives:

- **Objective 1.** Determining environmentally friendly, techno-economically feasible coal fuel gas cleaning technology for small-scaled fixed-bed type coal gasifier.
- **Objective 2.** Evaluation of the suitability of REACH regulation for any chemical risks involved in the extraction of trace elements from ash resulting of processes of coal gasification or coal combustion.

The methodologies used throughout the research period for both objectives were same in terms of obtaining literature data. These obtained literature data were analyzed further to reach the set objectives. However, obtained literature data were handled differently depending on nature of the pre-defined objective. The clear methodology path that brought to the each conclusions justifying to the objectives are outline below separately:

**Objective 1:** In order to reach objective number one, a complete first phase of an industrial technology innovation cycle was performed, which involved following stages:

- Initial idea- Innovative coal fuel gas cleaning method for small scaled coal gasifier
- Literature screening - Literature research on various coal fuel gas cleaning methods. For this, research papers, presentations and reviews were obtained through search engines, such as google ([www.google.com](http://www.google.com)), Science direct ([www.sciencedirect.com](http://www.sciencedirect.com)) and Web of science ([www.webofknowledge.com](http://www.webofknowledge.com)).
- Technology selection – Based on reviewed literature data, possible and innovative technologies that were thought to be suitable for small-scaled fixed-type gasifier were selected.
- Process modeling – Based on the selected innovative coal fuel gas cleaning technology, process modeling was done with the help of Aspen plus chemical engineering software. For that, the process simulation for the fixed-bed type coal gasifier and selected innovation fuel gas cleaning technology were done. This allowed, whether the selected innovative fuel gas cleaning technology were compatible for small scaled fixed-bed type coal gasifier.
- Techno-Economical analysis – After making sure that the selected innovative gas cleaning technology was suitable for target coal gasifier with help of process modeling, it was further analysed in terms of economics. Investment estimates for the electricity generation plant via fuel gas were done with highest accuracy. For that, Chinese e-commerce platform Alibaba ([www.alibaba.com](http://www.alibaba.com)) were utilised to obtain actual quotations for the different equipment and process plants. This allowed, economic analysis of whether investment for the proposing technology developed should be made or not.
- Market research – Process modeling and Techno-Economical analysis determined that proposing fuel gas cleaning technology is technologically and economically feasible to invest and develop the technology. Then, the market study for such technology in developing countries was conducted. For the market study, energy data relating to chosen particular countries were obtained from their energy ministry official website and from International Energy Agency ([www.iea.org](http://www.iea.org))
- Intellectual property generation/protection – Intellectual property generation for the proposing fuel gas cleaning technology was made and were applied for patent application via the Air-

Liquide Global E&C. Prior to that, patent search using patent search engine Google ([www.google.com/patents](http://www.google.com/patents)) and Patbase express ([www.patbase.com/express/search\\_basic.asp](http://www.patbase.com/express/search_basic.asp)) to make sure that patent for proposing technology does not belong to anyone or a company.

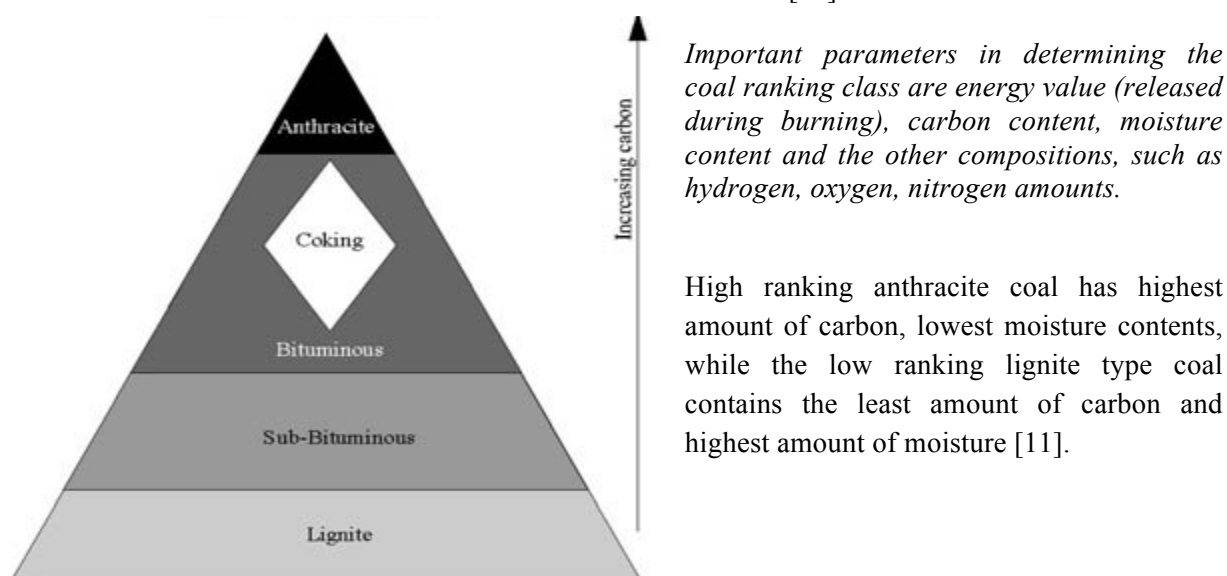
**Objective 2.** In order to reach the objective number two, a broad literature research was conducted. For the literature research, search engines such as Google ([www.google.com](http://www.google.com)), Science direct ([www.sciencedirect.com](http://www.sciencedirect.com)) and Web of Science ([www.webofknowledge.com](http://www.webofknowledge.com)) were used. To reach the objectives, the literature research was conducted systematically and involved the following stages in following orders:

- General review on coal combustion or gasification ash production and their commercial applications in Europe.
- Literature review on trace elements in raw coal and data analysing to determine feasibility of extracting trace elements from the coal combustion or gasification ash.
- Studies on commercially operating trace elements of any type extracting plants from coal combustion or gasification ash.
- Partitioning behaviour of trace elements found in coal were studied to determine which of the originally found trace elements in the raw coal can be found in fixed-bed gasifier bottom ash and in flash ash from the particulate matter removal system.
- Literature research were carried out to determine world average trace elements content in world coal, hence availability of trace elements via ash recovery process from annually consumed coal in Europe were quantified.
- Quantification of trace elements available for recovery process from the ashes resulting from annually consumed coal in Europe enabled to determine which EU regulation such process is subject to.
- Literature review on EU regulations relating to trace elements recovery from coal ash was conducted, in which Waste directive and REACH regulations were considered.

### 3. CONTEXT

#### 3.1. COAL

Coal is a world's most abundant and widely distributed combustible, sedimentary, organic fossil fuel formed through coalification process over millions of years. Coal formation started during the Carboniferous period (first coal age). Impact of high pressure and heat on accumulated decayed plant materials lead to the coalification process resulting in coal, which mainly consists of carbon, hydrogen and oxygen. The Coalification process has an important effect in the classification of coals into different groups as the process impacts the coal's physical and chemical properties. Coal classification is often referred as coal ranking and the original organic material exposed to heat and pressure for longer period of time belongs to higher ranking in the classification. Higher ranking is an indication that the coal has more carbon content per unit of weight compared to the low ranking coal. Therefore, organic maturity of the original plant material to transform them into carbon determines the coal ranking. Thus, the coal ranking varies from coal with least carbon content (lignite-brown coal) to coal with highest carbon content (anthracite). Between these extremes, sub-bituminous, bituminous coal belongs in the ranking. Figure 1 below demonstrates the coal ranking as a function of carbon content increase [10]:



**Figure 1: Coal ranking [11]**

According to the International Energy Agency's coal information, the total proven reserves of the world are 1,000 billion tonnes and are spread over more than 70 countries across the globe [2]. Coal is recognized as a high priority component for many country's energy strategy and is alternative energy source over gas and oil. Available coal source is enough to supply energy demand for 150 years, considering the current production rate of coal. Up until oil became competitive over coal in late 1960s, coal was the main energy source and as of today the majority of the produced coal is used for electricity generation, while some amount is used to provide fuel for residential building heating. Ranking of the coal determines, which applications it is utilized for. 40% of the world's electricity is generated from lignite or sub-bituminous type coal via coal fired power plants. Bituminous and Anthracite types coals are mainly used for cement, iron/steel manufactures and for domestic industrial purposes [11].

However, increased awareness of pollution, safety issues related to coal utilization and strict clean air policies/regulations (CO<sub>2</sub> emission), are encouraging the world to consume as less coal as possible.

At the same time, it is leading to increased interest and researches in order to develop clean coal conversion technologies. The aim would be to solve health and environmental problems. Successful development of clean coal technologies would lead to:

- Increased coal conversion efficiency
- Contribute to reduction in greenhouse gas (CO<sub>2</sub>)
- Reduce coal related pollutions.

Coal gasification is recognized as a one of the clean coal utilization method and has been at the spotlight in coal conversion industries due to its process efficiency and environmental friendliness compared to conventional methods. However, through coal gasification unwanted coal pollutants are released and they pose various problems. Pollutants from coal gasification and the problem they pose they pose to health are summarized below on table 1:

**Table 1: Toxic pollutants from coal burning/gasification and associated health problems [12]**

<b>Toxic coal pollutants</b>	<b>Health problems</b>
Dioxins, Furans	Cloracne, reproductive, developmental problems, damages the immune system, interfere with hormones and also causes cancer
Sulphur oxides	Asthma, chronic bronchitis, airways inflammation, eye irritation, psychic alteration, heart failure
Nitrogen oxides	Damages cell membranes in the lung tissue, causes constriction of the lung way passage, nasal irritation and pulmonary discomfort is common
Arsenic	Induces reactive oxygen species (ROS) and oxidative stress. Binds to thiols, alters signal cascade, imbalance in antioxidant levels. Triggers apoptosis and cell death, nausea, decrease in production of red and white blood cells, sensation of pin and needles in hand and feet
Chromium	Nose ulcers, skin ulcer, asthma, shortness of breath or wheezing, allergic reactions leading to severe redness and swelling of skin, long term exposure leads to damage of kidney, circulating and nerve tissues as well as skin irritation
Copper	Gastrointestinal: metallic taste, nausea, vomiting, gastrointestinal bleeding, Renal: haematuria, oliguria, elevated urea, creatinine and acute tubular necrosis
Cadmium	Gastrointestinal symptoms: nausea, vomiting, abdominal pain, diarrhoea, salivation, tenesmus, haemorrhagic gastroenteritis, may result in pulmonary fibrosis, headache, cadmium fume pneumonitis, hepatic necrosis, Renal necrosis, cardiomyopathy, chills, weakness and dizziness
Lead	Damages the brain and kidney, in pregnant women, high level of exposure may cause miscarriage, high level exposure in men can damage the organs responsible for sperm production
Mercury	Exposure to high level can permanently damage the brain, kidney and developing foetuses, effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing and memory problems
CO <sub>2</sub>	Higher concentrations can affect respiratory function by displacing the oxygen in the air and will lead to suffocation. Due to less available oxygen, nausea, vomiting, collapse, coma or even death can occur.
Tar	Exposure to coal tar is associated with an increased risk of skin, lung, bladder, kidney and digestive tract cancer.

Technology advancement has offered partial solution to tackle these health causing coal pollutants and there still exists problems from environment, health and process point of view. Therefore, coal



gasification process and gasification process associated problems will be closely looked at in the following sections.

**3.2. COAL GASIFICATION**

The gasification process was originally discovered in 1699 by Dean Clayton and the process utilization started back in the nineteenth century to produce fuel gas for heat generation purpose[13]. The very first fuel gas producing plant through coal gasification was built in London in 1812. Coal gasification is a chemical process that converts any material containing carbon into synthesis gas, mainly consists of carbon monoxide and hydrogen (commonly referred to as syngas). Utilization of coal gasification process were further advanced when Fischer-Tropsch process in 1923 were discovered by Franz Fischer and Hans Tropsch. This invention allowed converting coal into liquid fuel (Diesel, Gasoline) through gasification. Throughout the World War II period, much effort was paid in order to improve the gasification process to convert the coal into fuels and chemicals. However, after the war period, coal gasification process became less useful due to cheap fossil fuel availability. But, it still plays as interesting alternative for energy due to current status of conventional fossil resources and fuel price fluctuation. Gasification does not only apply for coal, but wastes and biomass can also be gasified. Gasification process in relation to coal combustion is a fairly new process as coal combustion has been used for a long time, dominantly to produce electricity by combusting. Combustion is a full oxidation of the coal, while the gasification is a partial oxidation process. Coals are combusted/gasified for different reasons and their distinctive differences are summarized below on table 2:

**Table 2: Differences between conventional coal combustion and modern gasification processes [14]**

	<b>Combustion</b>	<b>Gasification</b>
Chemical process	Full oxidation	Partial oxidation
Chemical environment	Excess air (O <sub>2</sub> )-oxidizing	Limited oxygen-reducing
Main product	Heat-Steam	Syngas ( CO and H <sub>2</sub> )
Downstream product	Electrical power	Electrical power, Chemicals, Fuels, pure H <sub>2</sub> and Fuel gas
Dominant application	Coal fired Power and Thermal plant	Chemicals, Fuels and SNG
Emission	SO <sub>2</sub> , NO <sub>2</sub>	H <sub>2</sub> S, HCN, NH <sub>3</sub> , COS
By-products	None	Sometimes – Depending on gasifier and feedstock

**3.2.1. Gasifier types**

Variety of gasification technologies have been developed within the last few decades to process different feed stocks starting from biomass to coal. The gasification process is quite sensitive to the feedstock type and the operating parameters. Therefore, strict maintenance and control of the process parameters are the key to high conversion of desired feed stock for that particular selected gasification technology. The level of impurities in the product gas or formation of unwanted by-product are controlled by the design of selected gasifier types, feedstock properties and the gasifier processing conditions (gasification agent, introduction of feed, oxidants ect). The coal gasification processes are most commonly grouped according to their bed type, which are 1) Fixed-bed 2) Fluidized bed and 3) Entrained-flow[14].

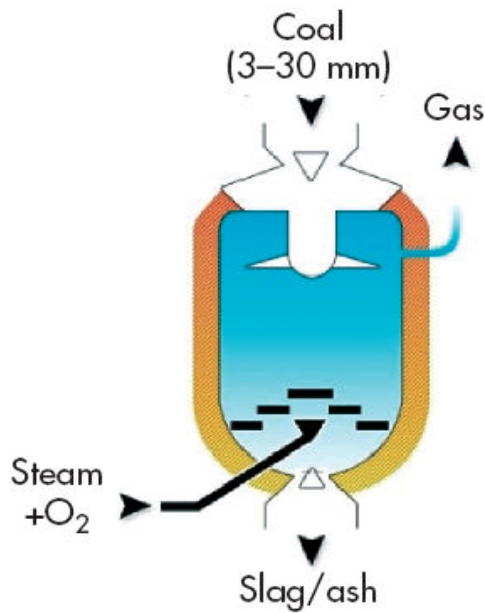


Figure 2: Fixed-bed gasifier [16]

should be carefully screened to fulfill the particle size requirement. However, the low exit temperature of the syngas leads to considerable amount of tar (complex mixture of hydrocarbons), as the formed tars in the pyrolysis zone gets carried upward by the flowing hot gas stream (pyrolysis zone is very close to the exit zone). Therefore, the syngas formed from this type of gasifier will need more gas cleaning before supplying the gas to intended applications. Caking coal as feed requires additional installation of stirrer in order to avoid the clogging of the bed [19]. Figure 2 above shows the working principle of the moving bed type gasifier:

**Fluidized-bed-gasifier:** The oxidizing agent for this type of gasifier is introduced from the bottom and flows upward. This flow expands the fixed bed of fine solids. Compared to fixed-bed type gasifier, the particle size of the feed coal is much lower. The bed expansion is controlled by the velocity of the gas sent through the bed. High gas velocities can cause the bed to expand throughout the entire reactor volume and leads to entrainment of solid particle from the reactor. For that, installation of hot cyclone at the downstream of the gasifier is needed, such that the solid fractions can be captured and recycled. This type of gasifier result in syngas with much better quality (less tar-reducing the need for gas cleaning). However, use of hard coal is limited as the carbon conversion is less and significant amount of un-reacted carbons are formed in the ash. Increase of gasifier temperature for better carbon conversion is constrained by the ash-softening temperature as going higher leads to fouling or the de-fluidization. Syngas from fluidized bed gasifier contains intermediate tar levels. The process control must be attained in

**Fixed-bed-gasifier :** It is also often referred as Moving-bed-gasifiers (up or downdraft) and larger coal gasifiers are often updraft due to gas distribution issues. The feed coal is supplied from the top while the gasification agents (Steam and Oxygen) are often supplied from the reactor bottom (counter-current flow). Then the coal slowly moves downwards as packed bed by gravity and carbon conversion in the coal occurs due to counter current upward flow of the gasification agents from the bottom. Such type of gasifier uses least amount of oxygen compared to other gasifier types as the heat transfer within the gasifier is efficiently arranged between feed and gasification agents to allow pyrolysis, drying and preheating. Stability of the formed coal bed regulates the low pressure drop across the gasifier height and for that the particle size of the fed coal

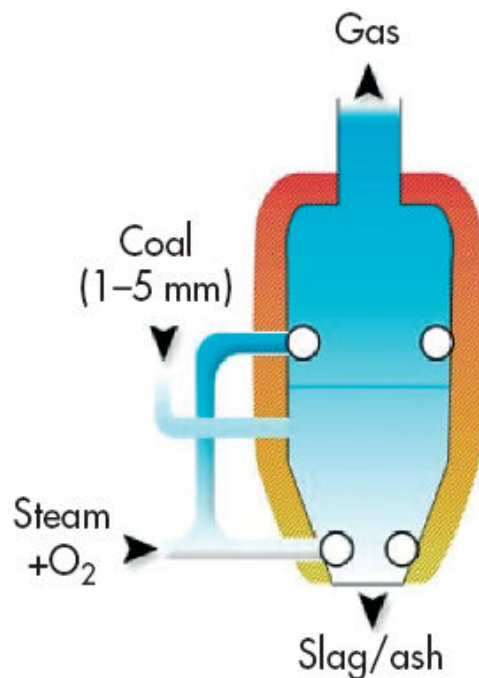


Figure 3: Fluidized bed gasifier[16]



order to maintain smooth fluidization. The heat exchange between the syngas exiting and ash leaving the gasifier as it is the case in fixed-bed gasifier cannot be regulated in fluidized bed gasifier as the rate of reaction in the middle of the reactor is very fast and turbulent circulating bed exists. Therefore, it is not possible to cool the syngas before exiting the gasifier and exit temperature is higher than that from the fixed bed gasifier.

**Entrained-Flow-Gasifier:** Operating conditions of these type of gasifiers are high pressure (86 atm), high temperature (>1300°C) and corrosive environment due to molten slag. The feed coal (pulverized) and the gasification agents (air/oxygen/steam) are fed co-currently to the gasifier top/bottom. Particles sizes of the feed coal are sufficiently small to be entrained in the flow. This type of gasifier consumes high amount of oxygen to create enough energy to keep the oxidation of the feedstock going, hence to melt all the ash content in the coal. This type of gasifiers has rapid carbon conversion (98-99%) due to high temperature, pressure and very small feed particle size within few seconds of residence time. Due to such instantaneous high reaction rate, the size of the entrained-flow-gasifier can be reduced. However, because there is no heat exchange between syngas leaving and co-flow of

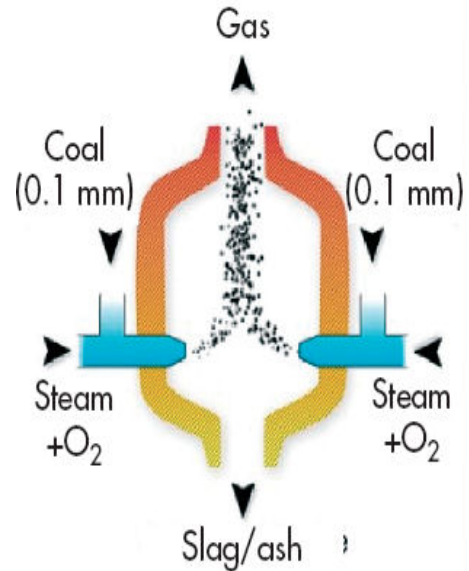


Figure 4: Entrained-flow-gasifier

feed and agent, the overall efficiency is lower compared to the moving bed type of gasifier. Therefore, optimization between low cost and high efficiency can be determined through economic analysis. Produced syngas is free of tar, oil, phenols or other contaminants that are formed from de-volatilization of coal inside the gasifier as they get converted to main syngas components ( H<sub>2</sub>, CO, CH<sub>4</sub>). Due to the operating conditions, such type of gasifier is able to process practically all type of coal to give tar free syngas. The table 3 below shows the summary of key parameters of the above covered gasifier types:

Table 3: Summary of different types of coal gasifiers commercially available [15]

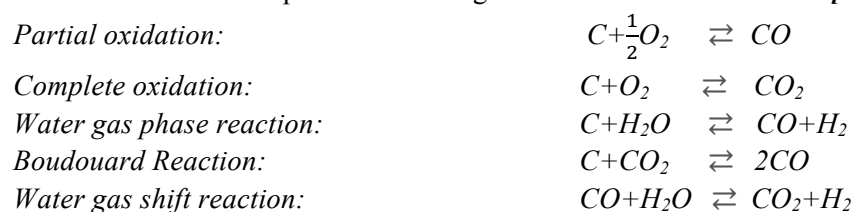
	Moving-bed	Fluidized-bed	Entrained-Flow
<b>Flow types</b>	Updraft (Counter current flow)	Stationary, circulating	Co-flow
<b>Feed size (mm)</b>	Coarse grain (3-60)	Small grain (0-6)	Pulverized (<0,25)
<b>Feed preparation</b>	Screening	Crushing	Grinding
<b>Feeding system</b>	Gravity	Gravity pipes, screw feeders	Dry or Slurry
<b>Preferred coal rank</b>	any	Sub-bituminous or lignite	Any
<b>Oxygen consumption (Nm<sup>3</sup>/kg<sub>daf</sub>)</b>	0,19-0,53	0,4-0,7	0,7-1,0
<b>Steam consumption (kg/ kg<sub>daf</sub>)</b>	2,0-0,4	0,2-0,6	0-0,3
<b>Syngas<sub>exit</sub> T (°C)</b>	350-800	800-1000	1300-1700
<b>Pressure (bar)</b>	1-100	1-40	1-86
<b>Carbon conversion (%)</b>	>95	80-95	>95

<b>Tar reforming</b>	Barely	Predominantly	Completely
<b>Residence time</b>	Hours	Minutes	Seconds
<b>Typical processes</b>	Lurgi FBDB <sup>TM</sup> , BGL	HTW(High Temperature Winkler), U-Gas, KBR Transport Gasifiers, KRW	Shell, GE energy, Siemens, E-Gas

Therefore, it can be said that the entrained flow gasifiers are suitable for good rank coal with low ash content and with low ash melting temperature. Low quality coal with high ash and melting temperature can be only gasified with fixed-bed gasifiers. Due to lack of industrial scaled reference for fluidized bed gasifiers, they are not favored.

### 3.2.2. Coal Syngas Composition

Gasification process is a thermo-chemical process which takes place at high temperature to convert the carbonaceous material coal into syngas, which is a mixture of H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub>. The chemical reactions that take place inside the gasifier is summarized below [16]:



The equilibrium reactions could proceed to either sides depending on the gasification temperature, pressure, and concentration of the reaction species. Therefore, through the above described gasification reactions, the product syngas consists of carbon monoxide, hydrogen, carbon dioxide, water-vapor and methane. Syngas quality, energy and efficiencies are influenced by process parameters (temperature, pressure, equivalence ratio, feed characteristics, and gasification agents).

The degree of equilibrium attained by the gasification reactions is dependent on the gasification temperature, which ultimately influences the volatiles in the produced syngas. Increase in temperature results more H<sub>2</sub> and reduction in CO, CO<sub>2</sub> and CH<sub>4</sub> [17]. However, such increase reduces the carbon conversion from feedstock to useful syngas components (H<sub>2</sub> and CO), as increase in temperature is achieved by supplying more oxygen, which CO<sub>2</sub> formation is increased. Therefore, optimal temperature should be selected to control the carbon conversion and desired syngas composition. Consequently, at high temperature syngas rich in H<sub>2</sub>, CO with small amount of methane and hydrocarbons are produced. On the other hand, low temperature results solid carbons and CH<sub>4</sub> in the syngas. Formation of solid carbons should be prevented by increasing the gasifier temperature to reform them as their presence deactivates the involved catalyst in the downstream units. Moreover, low gasification temperature results in the formation of tars, in which case the syngas containing tar should be treated for tar removal before it gets sent to its intended applications. Temperature increase helps to crack the tars into syngas or lighter hydrocarbons through thermal cracking process. However, the temperature of the gasification temperature cannot be freely controlled to thermally crack the tars as the operating window of the gasification process is limited by the ash properties of the coal. Depending on the bed-types as described above, the operating window is either below the ash fusion temperature (temperature at which the ash starts to deform, i.e., soften, or completely deform or fuse into a blob) or slightly higher than the ash fusion temperature, such that the desired bed-types are formed. Therefore, although high

temperature favors tar cracking, it is constrained due to the gasification operating window of the gasifier.

Effect of pressure increase reduces the H<sub>2</sub>, CO in the syngas, while formation of methane with CO<sub>2</sub> is increased. Therefore, higher quantities of CH<sub>4</sub> and CO<sub>2</sub> are produced at the same operating temperature than the un-pressurized operation. Another advantage of pressurized gasification operation allows for a smaller reactor vessels, piping, hence reduced capital cost for the gasifier and operating costs for the downstream applications as pressurizing syngas is lot harder than pressurizing the gasification agents for the pressurized gasifier.

When selecting the gasification agents, required syngas composition and energy should be taken into account. Common gasification agent choice for commercial gasifiers are steam, and oxygen. In coal chemical industries, oxygen supply for gasification agent comes mostly from the oxygen cryogenic separation plant, which the process involves cooling of the air down and distilling the oxygen out from the nitrogen. At this point, the oxygen is in liquid form, which is fairly easy to compress it to the chosen gasifier pressure. Air as gasification agent yields syngas with low calorific value (CV) because of the dilution with nitrogen. Use of steam as gasification agent (endothermic reaction) results product gas with medium calorific value rich in CO and H<sub>2</sub>. Oxygen either pure or from air as gasification agent in gasification process is needed in order to achieve the required temperature, while steam is needed to moderate the temperature in the gasification. Therefore, CV of the syngas is dependent on the gasification agents and their effect is shown below on table 4:

**Table 4: Effect of gasifier gasification agent on heating value of the produced syngas [17]**

Low CV	4-6 MJ/Nm <sup>3</sup>	Air/Steam
Medium CV	12-18 MJ/ Nm <sup>3</sup>	Oxygen/Steam

Primary product of gasification process is a synthesis gas containing mainly CO and H<sub>2</sub>. Depending on the fed material (different ranking coals, biomass, wastes, plastics), other components (CO<sub>2</sub>, CH<sub>4</sub>, Water vapor, H<sub>2</sub>S, Ethane and Tar ) can be formed.

Apart from the process parameters that influence the gasification performances, properties of the feedstock are equivalently important. Thus, energy, moisture content, volatile matter, ash content and its chemical composition, reactivity, size distribution, bulk density and Char properties of the feedstock should be carefully controlled, such that the gasifier performance is at its fullest is reached to give syngas of desired quality.

Choice of gasifier type for this research work is Fixed-Bed gasifiers. The gasifier was developed by Lurgi GmbH in cooperation with University of Berlin in early 1930 in the Hirschfelde pilot plant in Saxony, Germany for the purpose of producing what is known as fuel gas. The first full scaled commercial plant was built in 1936 at Bohlen, Saxony Germany. Then, various scaled (bench and pilot) units were built and run to generate gasifier performance data as a function of various coals and different designs. This included [18]:

- Testing of Alabama caking coals at bench scale units of 4, 6 and 13,5 inches at the Central Experimental Station of the Bureau of Mines in the USA in 1946.
- Testing of high volatile and weakly caking coal at the pilot plant built at Holten, Germany in 1953
- 170 MW combined cycle plant based on FBFB gasifier at Lunen, Germany in 1973

As a result of these test works, the fixed-bed gasifier concept were developed further that the gasifier can gasify various types of coal, including bituminous coal. The gasifier concept advancement resulted several distinctive Lurgi FBDB™ gasifier versions. They are the Mark II, Mark III, Mark IV and Mark VI gasifiers. The latest version of the Mark series is the MK-plus. These advancements included increased gasifier diameter from 2,6 meters to 4,7 meters, together with increased processing gasifier capacity [19]. Main physical differences of MK-plus version in relation to the previous gasifiers is increased diameter to 5,05 m, increased height from 12,5 to 17 and operational capability at high pressure as 40-60 bar [20, 21]. Therefore, Lurgi FBDB™ gasifier has been used worldwide to generate syngas for various purposes as the gasification technology has shown its versatility and efficiencies in many areas over the past decades. This allowed supplying of the gasification technology to world’s major coal gasification projects. The technology owner (licensor) of the Lurgi FBDB™ Gasifier is the international industrial gas company Air Liquide. Air liquid was founded in 1902, is a global leader in industrial and medical gases and related services with nearly 50,000 employees in 80 countries serving more than 2 million customers[22]. The group produces air gases (Oxygen, Nitrogen, Argon, and Hydrogen) through their constantly innovated technologies. On 20<sup>th</sup> July, 2007, Air-liquide purchased engineering firm Lurgi AG and this acquisition broadened the technology portfolio of Air Liquide’s Engineering and Construction division[23]. This includes Coal-to-Liquids (CTL) and Coal-to Chemicals (CTC) technologies, apart from the Hydrogen and synthetic gas production technologies.

The main role of the gasifier is to gasify coal under pressure in the presence of high-pressure steam and pure oxygen to generate syngas composing of hydrogen and carbon monoxide, methane and carbon dioxide. The gasifier consist of lock hopper system at the coal entrance for the purpose of feeding the gasifier with coal and move it through the gasifier length and another lock hopper system at the bottom of the gasifier to remove ash. As it was explained above in the fixed-bed gasifier concept (updraft), the entering flows are in counter current flow and installed rotating grates at the bottom of the gasifier are used to regulate the gasification agents (steam and oxygen) to efficiently promote gasification reaction and to even/gentle withdrawal of ashes to support coal bed inside the gasifier. At the bottom of the gasifier, the temperature is around 300-400°C, while it is 500°C at the top. The gasifier creates temperature gradient in the gasifier due to heat exchange between syngas exiting-feed-coal and Ash exiting-gasification agent entering [24]. The temperature gradient is shown below on figure 5:

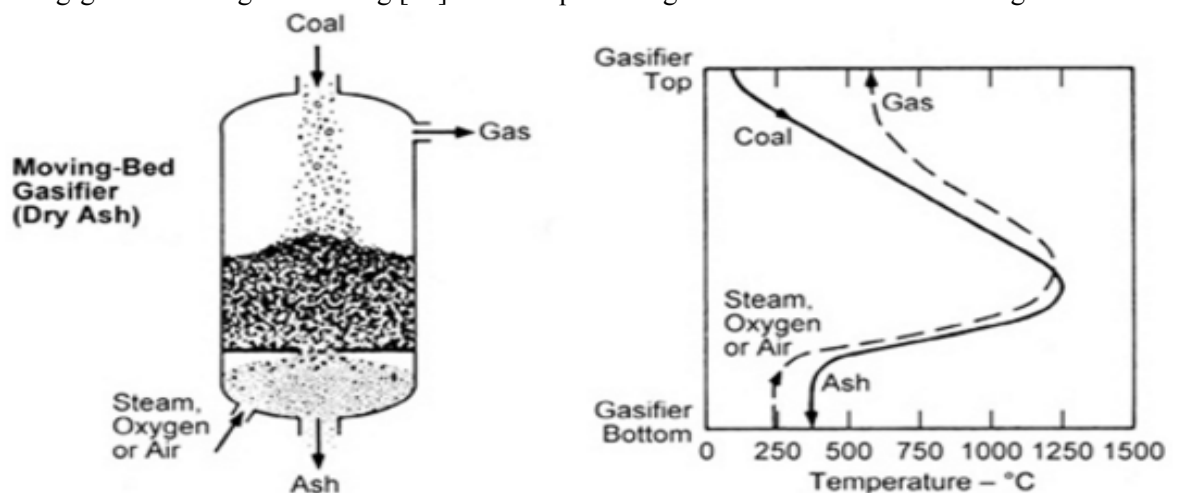


Figure 5: Temperature gradient of fixed-bed gasifier[25]

The fixed-bed gasifier also consists of quenching system near the syngas outlet and its role is to quench the raw gas ( un-reacted steam, oxygen, tars, phenol, dust, sulfur compounds, NH<sub>3</sub>, HCN) with recycling water. The gasifier uses water jacket for the purpose of cooling the gasifier vessel and steam generated makes up small portion of the needed steam as gasification agent.

It is estimated that there are more than 100 Lurgi FBDB gasifiers operating around the globe and majority of them are Mark IV series installed in South-Africa, USA and in China, which are [26, 27]:

1. Sasol’s Coal-to-Liquid plant producing liquid fuels (Diesel, Gasoline) via Fischer-Tropsch method in Secunda, South-Africa (2\*40 Mark IV units gasifiers generating 3,3 mmNm<sup>3</sup>/h) consuming over 1 billion tonnes of coal are installed – Started up in 1977
2. North Dakota’s Coal-to-Natural gas plant in the USA. 14 Mark IV units are installed for the gasification
3. Large number of Lurgi gasifiers (50) across China generating syngas for various applications
4. Coal gasification island in India (7 Mark IV gasifiers producing 225,000 Nm<sup>3</sup>/h of syngas)- Started up 2014

Having covered the possible type of gasifiers, the advantages and disadvantage of fixed-bed gasifiers against the other types of gasifiers can be outlined as follows:

<b>Advantages:</b>	<b>Disadvantages:</b>
<ul style="list-style-type: none"> <li>• Relatively low air (oxygen) is required</li> <li>• Heat recovery equipment is not needed due to counter flow design</li> <li>• High methane formation</li> <li>• Feed flexibility</li> <li>• Suitable for low quality coal with high ash, moisture and ash melting temperature</li> <li>• Coarse particle size</li> </ul>	<ul style="list-style-type: none"> <li>• Fine coals cannot be used</li> <li>• Requires gasification modification for caking coals</li> <li>• Tar-Oil-Naphtha (Hydrocarbon liquids) are produced but can be valorized as products.</li> </ul>

At the end of gasification process, all the carbon atoms should be gasified and no oxygen or steam should be present.

### **3.2.3. Coal Syngas applications**

Gasification adds value to low (coal) or negative (petroleum or coal wastes) value feed stocks by converting them to valuable and flexible coal syngas. Syngas is a gasification process product and is a mixture of hydrogen, carbon monoxide, carbon dioxide and very often small amount of methane. Syngas generated through available technology in the coal gasification industry can be used in broad, sophisticated array of products production. Moreover, fuel gas primarily consists of hydrocarbon (methane), hydrogen and carbon monoxide. Due to hydrocarbon content in the fuel gas results fuel gas with higher heating value than the syngas as the syngas contains less amount of methane. Therefore, their applications vary due to their composition.

### Power generation

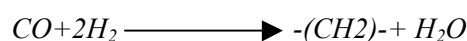
Syngas resulted from coal gasification is a combustible gas and can be converted into electricity with help of all prime movers from steam cycles to gas engine/turbines or even combined cycle. However, from the capital cost point of view, power generation through coal syngas is problematic and is not always attractive end use.

### Liquid fuels

Another alternative for coal syngas utilization is in production of transportation fuels through commercially available technologies. Coal syngas can be converted into liquid fuels (Diesel, Gasoline) via Fischer-Tropsch or via Methanol (Methanol-to-Gasoline) route.

### Fischer-Tropsch (F-T) process-For Diesel and Gasoline production

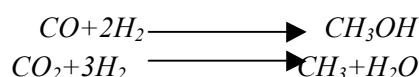
Fischer-Tropsch (F-T) process involves reacting of one mole of CO with two moles of H<sub>2</sub> resulting mainly paraffin straight chain hydrocarbons and alcohol. F-T is exothermic reaction and takes place at 200-350°C, at pressure between 20-60 bars with help of catalyst. For high temperature F-T (330-350 °C, 25 bar) an iron -based catalyst is used, while iron or cobalt based catalyst is used for low temperature (220-250°C, 25-60 bar ) F-T process. Low temperature F-T process gives Diesel fuel as end product with syngas conversion rate percentage of 60-93%, while High Temperature F-T process gives Gasoline with conversion rate of 85%



Impurities (NH<sub>3</sub>, HCN, H<sub>2</sub>S, COS) in the raw syngas poisons the F-T process catalysts and they should be removed or lowered to required level for the process [28]. Iron based catalysts in relation to cobalt based catalyst has high Sulphure tolerance, available at lower cost and has selectivity towards olefin products and alcohols. On the other hand, Cobalt based catalyst offers longer life (>5 years) [29] and reactive for hydrogenation and has low selectivity towards olefins (unsaturated hydrocarbons) and alcohol. Therefore, process conditions should be set, such that side reactions, such as methanation , Boudouard reaction, coke deposition , catalyst poisoning does not occur.

### Methanol-To-Gasoline (MTG) route

In order to produce Gasoline, syngas is first reacted catalytically to make methanol. Carbon monoxide, Hydrogen and Carbon dioxide are reacted according to below shown chemical formula:



To convert the syngas into methanol at maximum efficiency, side reactions should be unfavored to eliminate by-products, such as methane, higher alcohols, di-methyl ether (DME). The reactions are exothermic and a low temperature, high pressure are favored for methanol production. There are different methanol production technologies available, depending on the operation pressure. High pressure process ( 250-300 bar) uses zinc chromium oxide catalyst (>340°C) and low pressure process ( 50-100 bar) uses copper-zinc-chromium catalysts. The main differences between these processes are in operating pressure, used catalyst, hence the reactor design due to demand for heat recovery from exothermic reactions and to control the temperature. Low pressure process requires lower capital, production costs and operation reliability and are widely used for methanol production[30]. Produced methanol can be further processed in Methanol to Gasoline units for gasoline production.

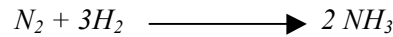
### Chemicals

Syngas are building block for production of various chemicals from Ammonia for fertilizer production to synthetic natural gas.



**Ammonia production**

Majority of the produced ammonia worldwide are utilized for fertilizer production, followed by small portion for various other applications. For ammonia production, 1 mol of nitrogen gets reacted with 3 moles of hydrogen under process condition of 350-550 °C, 100-250 bar and iron-based catalyst according to below equation:

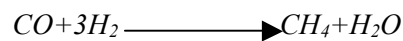


Majority of the nitrogen atom in the industrially produced chemicals are often derived from ammonia, such as in plastic, polyurethane and polyamides production. Moreover, apart from use of ammonia in fertilizer, ammonia is used for mining explosives production.

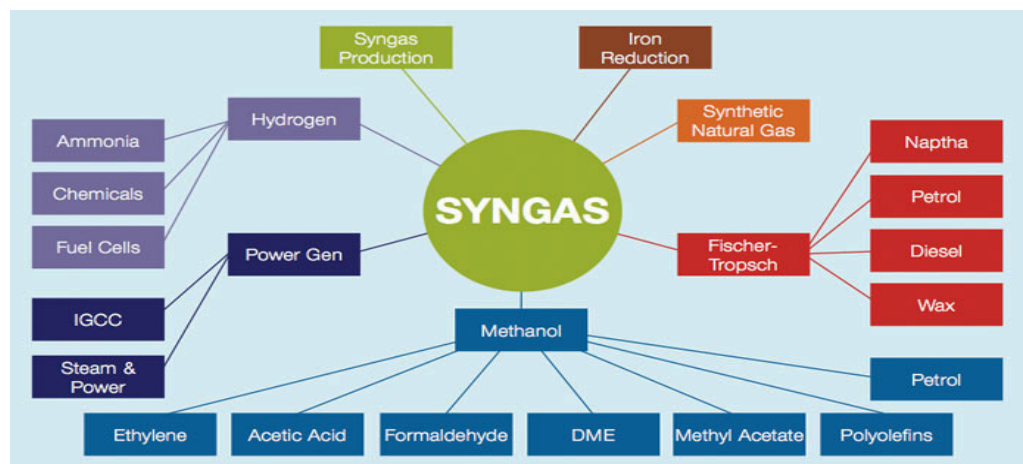
Ammonia production from coal-based syngas containing oxygen gases (CO or CO<sub>2</sub>) has restriction. For example, oxygen gases in the syngas has to be lower than 20 ppmV [30]. However, the commercially proven cleaning technologies offer solution to meet such requirements.

**Synthetic natural gas (SNG)**

Synthetic natural gas (SNG) is a combustible gas that has similar properties to that for natural gas. Syngas from coal gasification process can also be used for SNG production. One mole of carbon monoxide is catalytically ( high nickel content) reacted with 3 moles of hydrogen to make methane and water according to below shown reaction:



Methanation reaction is very exothermic and heat release should be taken into consideration. Depending on the composition of coal syngas, further process for syngas component ratio change should be made and initial compositions depend on various parameters during gasification as discussed above. Furthermore, coal syngas can be the basis to various other products and applications and summary of syngas application can be briefly demonstrated with help of the chart below:



*Figure 6: Applications of syngas [31]*

However, the raw syngas exiting the gasifier has to go under several stages for unwanted impurities removal depending on their intended end applications. Then the resulting clean syngas is suitable for a number of applications including liquid fuels, chemicals, fertilizer, energy, electricity ect.

### 3.2.4. Syngas quality requirements

Coal gasified syngas contains other impurities apart from the main necessary components (H<sub>2</sub>, CO) due to the nature of the coal. Unwanted impurities should be removed before it is used for mentioned examples. Depending on the suitable or intended applications, the degree of removal or cleanness of the syngas varies. There is many literature data available from research and development activities conducted within the coal conversion work scope. For this research work, Fixed-bed type gasifiers are chosen and one of the biggest disadvantages are production of tar in the syngas due to state of the technology. Followings are the few estimates of tar tolerance threshold of the end use equipments [32]:

- Compressors accept syngas containing tar within 100-500 mg/Nm<sup>3</sup>.
- Internal combustion engine (ICE) has different tolerances thresholds depending on amount of light or heavy tars present. For example, for light tars the maximum tolerance is 50 mg /Nm<sup>3</sup>, while it is only 5 mg/Nm<sup>3</sup> for heavy tars.
- Gas turbines have much higher requirement for syngas tar limit, it should be lower than 0,1 mg/Nm<sup>3</sup>.
- For F-T process, the tar content should be below 0,1 mg /Nm<sup>3</sup> and concentration of solid particles lower than 0,02 mg /Nm<sup>3</sup>.

**Table 5: Gas quality requirement for power generation [33]**

Component	Unit	IC engine	Gas turbine
Particle	mg/Nm <sup>3</sup>	<50	<30
Particle size	μm	<10	<5
Tar	mg/Nm <sup>3</sup>	<100	
Alkali	mg/Nm <sup>3</sup>		0,24
CO <sub>2</sub>	Vol %	No limit	No limit

**Table 6: Acceptance and preferable fuel gas specification for modern engines [34]**

Parameter	Acceptable	Preferable
Dust content	<50	<5
Particle size	<10	<1
Tar content	<100	<50
Gas heating value (KJ/Nm <sup>3</sup> )	>2500	>4200

At the major coal gasification plants, there are external treatment units for raw syngas to meet their application requirements.



### 3.3. SYNGAS CLEANING METHOD AND TECHNOLOGIES

In the previous sections, it was shown that coal is gasified through different types of gasifiers for various application uses. Before utilizing the gasification product in its intended uses, the syngas should be cleaned to meet particular application's requirement and for environmental and health reasons.

For coal syngas cleaning, there are various technologies available, some are commercially proven, while some are at different stages of development. Before directly focusing on suitable coal syngas cleaning method for small-scaled fixed-bed gasifiers, general literature review on syngas cleaning as a whole were conducted. To summarize the literature review findings, the impurities in coal syngas can be divided into four main groups and available technologies for each groups can be summarized as follows:

**Table 7: Summary of coal syngas impurities and available technologies to clean [12]**

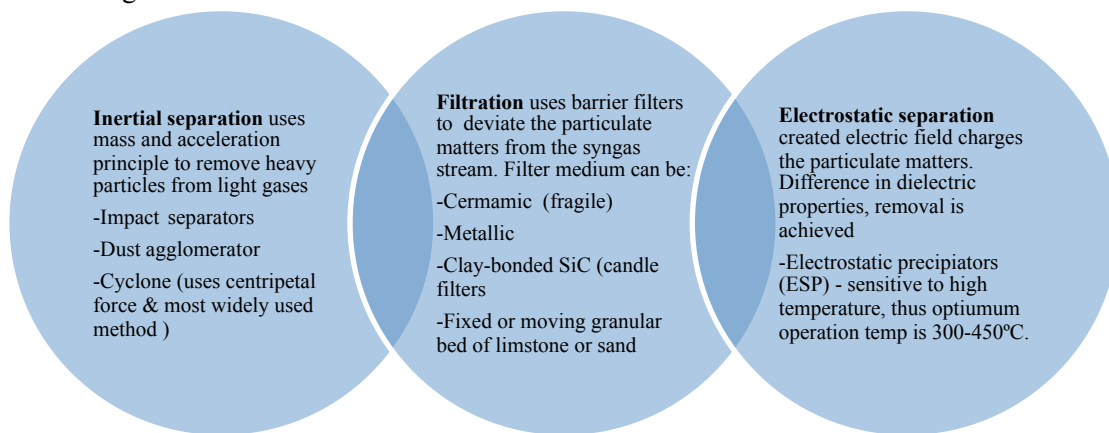
	<b>Impurities</b>	<b>Technology</b>
<b>1</b>	Solid particle	-Cyclones, reverse flow cyclones, Barrier/candle filters, metallic filters, granular bed filters (with Ni and MgO) -Electrostatic precipitator, Spray scrubber, impactor scrubber, venturi scrubber, electrostatic scrubber
<b>2</b>	Tar	-Thermal cracking -Catalytic cracking using Fe or Ni based catalysts or olivine or calcined dolomite, -Thermal plasma (Elevation of temperature much higher than that of the requirement in the gasifier) -Non-thermal plasmas (presence of free radicals, ions and other excited molecules create environment that decomposes tar molecules) <ul style="list-style-type: none"> <li>• Pulsed corona (Effective at 400°C)</li> <li>• Dielectric barrier discharges</li> <li>• DC corona discharges</li> <li>• RF plasma</li> <li>• Microwave plasma</li> </ul> -Nickel based candle filter -Oil based gas washer (OLGA) Venturi scrubber
<b>3</b>	Sulfur	-Physical and chemical adsorption, ZnO/FeO sorbents, use of catalysts like CoMo for COS conversion, nickel and iron based catalysts Lime/limestone injection LO-CAT technology Chemobiological process
<b>4</b>	Nitrogen	-Thermal catalytic decomposition of NH <sub>3</sub> using Ni and Zeolite as catalysts combined with MnO <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> , Tungsten based catalysts such as WC and WZ -Water scrubbing technique

In the following sections, these main four groups of impurities in coal syngas and suitable cleaning technologies for them are discussed further in details.

**3.3.1. PARTICULATE MATTER REMOVAL**

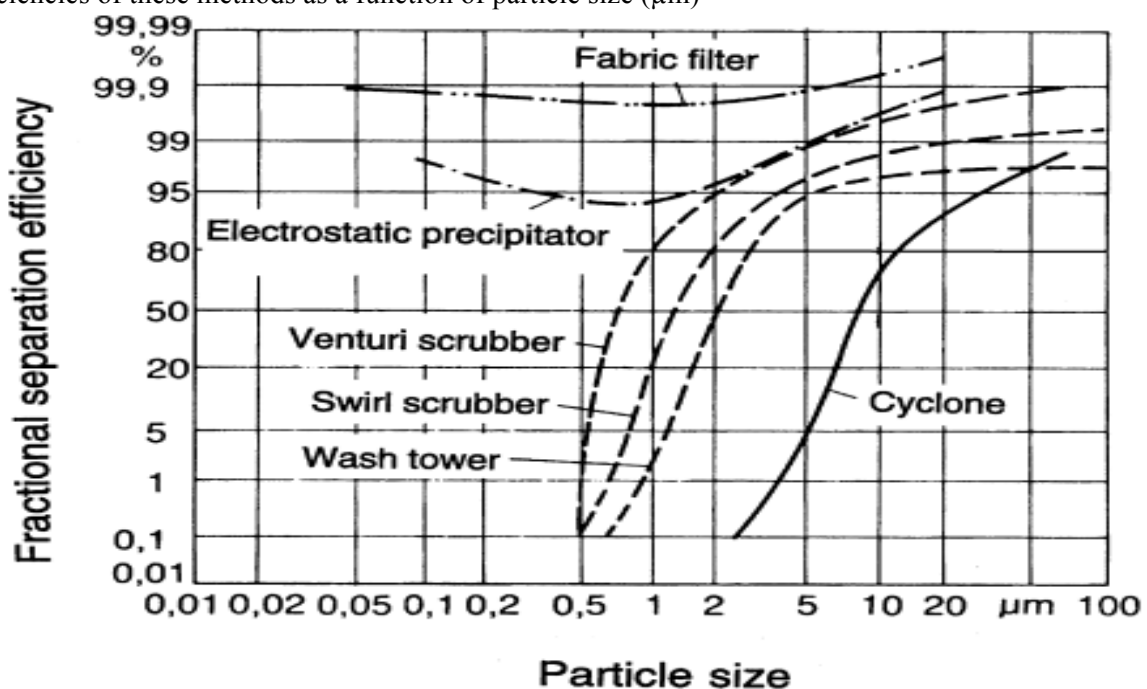
Particulate matter is one of the impurities formed when coal is gasified and range from less than 1 μm to more than 100 μm. Formed particulate matters are classified based on the aerodynamic diameter. Amount of particulate matters in the syngas and their sizes vary depending either on the type of coal fed and on gasifier design [35]. Removal of particulate matters from the syngas is mandatory as they cause abrasion, fouling, corrosion to downstream units and emission problems. There are various types of methods and technologies available to remove them and the current available technologies can be classified into hot and cold gas particulate matters removal.

Hot gas particulate matter removal technologies consist of inertial separation, filtering and electrostatic methods. Basic operational principles of these available technologies are summarized and shown below on figure 7:



**Figure 7: Brief summary of Hot gas particulate matter removal technologies [36-37]**

In the cold gas particulate matters removal, wet scrubbing (water based) technologies at ambient temperature are performed. This includes wet dynamic scrubbers, spray scrubber and electrostatic scrubbers. Cold gas particulate removal technologies are employed based on the particle size and they are often recommended when the size reaches 3 μm[38] . But, due to extra waste stream formed from water usage, it makes it un-favored option for particulate matters removal. Figure 8 below shows the efficiencies of these methods as a function of particle size (μm)



**Figure 8: Efficiencies of particulate matter removal technologies with change in particle size (μm) [39]**

### 3.3.2. SULPHUR COMPOUND REMOVAL

Syngas from coal gasification contains sulphur components and they are hydrogen sulphide ( $H_2S$ ) and carbonyl sulphide (COS). Presence of sulphur based compounds leads to metal surface corrosion and process catalyst poisoning. Concentration of these compounds depends mainly on sulphur in the feedstock. Depending on the application requirements, degree of sulphur based compounds removal varies. Some applications require very low levels of sulphur. Commercially available sulphur based compound removal technologies can be divided into hot and cold gas sulphur compounds removal [40].

**Hot gas sulphur compounds removal:** This method uses adsorption technique to remove sulphur based compounds by combining them with the adsorbents physically (weak van der Waal's intermolecular dipole interactions) and chemically (covalent bonding of adsorbate molecules). There are three essential steps for sulphur based compound removal starting from reduction of solid sorbent with the sulphur species, followed by sulphidation, where metal oxides (Zn, Fe, Cu, Mn, Mo, Co, V) react with sulfur and regeneration of step to recover the original metal oxides and enriched  $SO_2$  stream [41]. Then,  $SO_2$  stream gets sent further for sulphur recovers, where sulfuric acid or elemental sulphur can be produced. Sulphidation metals, such as Zinc and Copper oxides are abundantly available and are mainly used for sulphur removal. It offers 99% of sulphur removal.

Moreover, carbonyl sulphides are converted to  $H_2S$  using Cobalt-Molybdenum and nickel based catalysts. For this purpose, nickel based catalyst are favored as it stays active and stable with time, while stability and activity of Cobalt-Molybdenum catalyst decreases with time [42].

**Cold gas sulphur compounds removal:** In this method, chemical and physical solvents are used. In the chemical solvent method, it creates weak chemical bonds between amines (primary, secondary and tertiary) and acid gases. Chemical solvent method is not suitable for COS, hence requires the COS to be converted to  $H_2S$  before the chemical solvent method is used, because COS degrades chemical solvents, such as monoethanolamine (MEA) or diethanolamine (DEA). However, addition of fresh solvent is needed to compensate the solvent loss due to operation [43].

### 3.3.3. NITROGEN COMPOUND REMOVAL

Nitrogen compounds in the syngas from coal gasification are present as  $NH_3$  and HCN. Nitrogen compounds should be removed to avoid catalyst poisoning and to limit the nitrogen oxide emissions. The removal method can also be divided into hot and cold nitrogen component removal.

**Hot gas nitrogen compound removal:** This approach focuses on decomposing the nitrogen compound instead of removing them as a whole from the gas stream. However, ammonia produced from coal gasification process does not easily decompose and this requires catalytic oxidation or thermal catalytic oxidation. The catalyst to be used should have high selectivity towards oxidizing the nitrogen, hence to avoid side reactions.

In catalytic thermal decomposition,  $NO_x$  molecules are dehydrogenated to give N and H radicals, which will then recombine to give  $N_2$  and  $H_2$ . The typical catalysts for it are Nickel and Zeolite catalysts and highest conversion of  $NH_3$  with these catalysts are achieved at  $500^\circ C$  [44]. However, at this temperature, catalysts get deactivated due to CO induced coking. Therefore, the thermal catalytic reactions are carried out at  $600-800^\circ C$ .

**Cold gas nitrogen compound removal:** In this method, the fact of high  $NH_3$  solubility in water is taken advantage of and nitrogen compounds are removed by absorption in water.

### 3.3.4. TAR REMOVAL

Formation of tar in coal gasification depends of type of gasifier utilized and the coal type fed to the gasifier. These organic impurities vary from low molecular weight hydrocarbon to high molecular weight poly nuclear aromatic hydrocarbons. High molecular weight hydrocarbons are of interest as they polymerize or condense to more complex structures throughout the involved process pipes or heat exchangers. Such event results in fouling and attrition problems, which eventually lead to loss of overall plant efficiency and increase the plant's operation costs. There are commercially proven tar removal technologies for large scaled gasification plants, however use of these technologies for small scaled gasifiers are not suitable due to economical and technical constraints. Uses of small scaled gasifiers, in particular tar forming fixed-bed gasifiers are quite common in developing countries for fuel gas generation purpose. Lack of economical and environmental tar removal technologies in small scaled coal gasification leads to use of expensive anthracite or semi-anthracite. Therefore, development of economical and environmentally friendly tar removal technology for small scaled gasifiers will allow use of cheap widely available sub-bituminous coal and will allow use of fixed-bed gasifiers, such that the advantages of fixed-bed gasifiers can be possessed.

During the literature review on tar removal, it was seen not much literature was available for coal tar, but much could be found regarding the biomass tar removal from biomass gasification. Biomass gasifiers are similar in sizes to small-scaled coal gasifiers and tars from these cases would have similar behavior, but will have compositional differences. Therefore, review on tar removal also consists of biomass tar and their removal methods. The term organic impurity (tar) covers various complex compounds and tar in particular needs clear definition, the common term for biomass-based tar was determined by the members of the gasification task of the IEA Bioenergy. This included the US DOE and the GGXVII of the European commission and the meeting had decided to define tar as hydrocarbons with molecular weight higher than that for benzene and such definition is the most widely accepted definition for tars [45].

In addition, The Energy research Centre of the Netherlands (ECN), which is the largest energy research institute in The Netherlands has refined the initial biomass tar definition and made it more comprehensive through their classification approach. The classification focuses on the actual tar properties and its most typical components, hence pays close attention to the tar dew point rather than the actual tar concentration [46]. These classifications are shown below on table 8:

**Table 8: Biomass tar classification by ECN [47]**

Class 1	<b>GC undetectable tars</b> Including the heaviest tars that condenses at high temperature even at very low concentration	Gravimetric tars
Class 2	<b>Heterocyclic components</b> Components that shows high water solubility due to their polarity	Pyridine, phenol, cresol, quinoline
Class 3	<b>Aromatic components</b> Light hydrocarbons that are not important in condensation, but might cause problems concerning their solubility in water	xylene, styrene, toluene
Class 4	<b>Light polyaromatic hydrocarbons (2-3 rings PAH's)</b> They condense at high concentrations and at intermediate temperatures.	naphthalene, methyl-naphthalene, biphenyl, ethenyl naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene
Class 5	<b>Heavy polyaromatic hydrocarbons (4-5 rings PAH's)</b> Condense at high temperatures and at low concentration	fluoranthene, pyrene, benzo-anthracene, chrysene, benzo-fluoranthene, benzopyrene, perylene, indeno-pyrene,

Biomass classification allows determination of the tar dew points and point at which tars get problematic during the process (tar condensation). The tar dew point is the temperature at which the

total partial pressure of tar equals the saturation pressure of tar. Biomass tar dew point is in range of 150-300°C and reducing of the tar level is most crucial before the syngas reaches such low dew points. Class 1, 4 and 5 tars have impact on the tar dew point (easily condenses at high temperature), while the class 2 and 3 have less influence on the tar) [48].

Tar classification shown on table 8 above is for biomass tar. The age of the feeding material (coal is older than biomass) affects the quantity and type of tar formed in the gasification process. For example, coal tar is generally much more aromatic than biomass tar; meaning coal tar has lower H/C and O/C ratios. Therefore, coal tar can have much more rings than 4-5 rings. However as of today, there are no such type of coal tar classification as for the biomass and no details on how big coal tars are [48]. The basic behavior of the coal tar will be similar to that for biomass tar, but there will be differences due to their compositions.

### 3.3.4.1. Tar decomposition mechanism

The main reaction steps for biomass tar decomposition are:

- Radical-forming reactions-Breaking of chemical bonds
- Propagation reaction- New chemical bonds form
- Transfer of hydrogen
- Isomerisation reaction
- Termination reaction- Two radicals react with each other

The type of tar reforming product depends on the gas phase composition and possibilities are [49]:

- Decomposed tars may react with other tars resulting even larger tar molecule, hence soot in an inert environment. Therefore, radical formation does not guarantee tar decomposition as it could worsen the tar content
- Presence of H<sub>2</sub>O or CO<sub>2</sub> increases the rate of tar decomposition as the radical may react with H<sub>2</sub>O or the CO<sub>2</sub>.
- Presence of H<sub>2</sub> in the decomposition environment inhibits the decomposition rate
- In H<sub>2</sub>/H<sub>2</sub>O/CO<sub>2</sub> atmosphere, the tar radical reaction with H<sub>2</sub>O and CO<sub>2</sub> is suppressed by presence of H<sub>2</sub> as the tar radical would readily react with H<sub>2</sub> over H<sub>2</sub>O and CO<sub>2</sub>.

The tar decomposition mechanisms were studied by Jess in the presence of hydrogen and steam at temperatures of 700-1400°C with naphthalene, benzene and toluene as model compounds [49]. The residence time for these studies were short as 0, 2-3 seconds long and the experiment were conducted at varying hydrogen, steam and pressures. The results of the study showed benzene was the key component for tar decomposition and high temperature (1400°C) is needed to convert all the cracking products into the desired syngas components. Identified overall reaction mechanism of this study is shown below on figure 9:

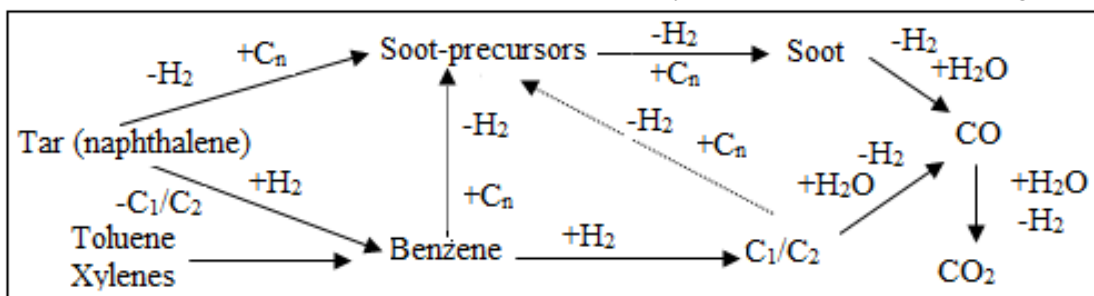


Figure 9: Tar reforming reaction mechanism in the presence of Hydrogen and Water [51,52]

### 3.3.4.2. Tar removal methods

A lot of effort is put by the researchers in the hope of developing most effective and economically feasible methods to reduce/remove the tars in the syngas. There are various

methods available, not yet commercialized to deal with the syngas tars and these methods are divided into 2 main categories (Primary and Secondary). The differences are the location of the tar removal process, if the tar is removed inside the feed gasifier; it is often referred as primary method. If the tar is removed outside the gasifier, it is the secondary method.

In the primary method, the tar is removed inside the gasifier with help of either additives or catalyst. More importantly, choice of the gasifier plays important role as it controls the vital parameters that affects the product distribution, such as: temperature, type of feed, pressure, gasifying agent and residence time. Therefore, selecting appropriate gasifier type for the selected feed and optimizing the gasifier configuration is the initial primary approach for tar removal [53].

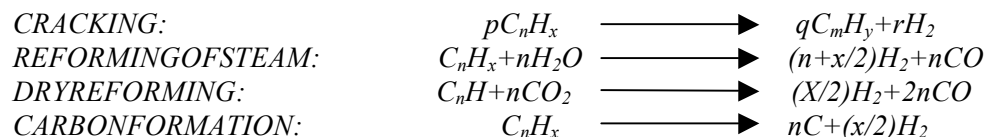
Increase of gasifier temperature results high carbon conversion and low tar content [14]. However, it was observed in biomass gasification cases that there are certain high temperature range at which different classes of tar gets produced. Therefore, increasing the gasifier temperature does not guarantee syngas free of tars [54]. The primary tar reduction measure in gasifier involves use of cost effective bed additives or catalyst and there are many studies available where different types of bed additives and catalyst are used. But because the aim of this investigation focuses on the secondary tar removal method, not much is covered here about the primary methods [55-57].

The secondary method employs separate gas cleaning unit and is located downstream of the gasifier. This method is further divided into subgroups of two. The first sub-group is physical method and such method usually requires lower operating temperature as the tars start to condense (below 450°C) in form aerosol in the gas stream. Formed aerosol then can be removed by physical methods as they are heavier than vapor. The available physical methods include: cyclones ceramic/fabric-filters, rotating particle separators, electrostatic precipitator and organic-liquid or water based scrubbing. However, because they produce additional stream (for wet cases), it would need an additional step to treat them and reduces the overall efficiency [53].

The second sub-group is the chemical method for tar removal, which are catalytic/thermal cracking and the plasma cracking methods.

**THERMAL CRACKING:**

This method uses high temperature (1100-1300°C) to crack the large organic compounds of the tars into smaller and non-condensable gases [58]. The tar removal efficiency depends on the temperature at which the tar is exposed to and the residence time. For example, naphthalene in tar would be reduced by more than 80% in 1 second at 1150°C, while the same result is achieved at 1075°C for 5 seconds. The thermal tar cracking occurs through one of below described mechanisms [59]:



The  $C_nH_x$  on above decomposition mechanism represents tar, while  $pC_mH_x$  is the hydrocarbons with smaller carbon number than that for the tar.

**CATALYTIC CRACKING**

For tar cracking in the syngas, there are several potential catalysts available and catalyst should possess following properties according to Yung et al [60]:



1. Effective removal of tar
2. Depending on the application of the syngas, the catalyst must be able to reform the methane content
3. Catalyst must be able to regulate the syngas ratio depending on its applications
4. Resistant to deactivation due to carbon fouling and sintering
5. Easy regeneration of catalysts
6. Should be strong
7. Must be not expensive

The tar removal catalyst are classified into 6 groups, which are Nickel based, non-nickel based, Alkali metal catalyst, Basic catalyst, Acid catalyst and Activated carbon catalysts. Brief descriptions of mainly used catalyst are explained in the following section with catalyst composition summary at the end of each section. The catalyst composition consists of 3 crucial components, which are an active catalytic phase or metal, a promoter to increase the catalyst activity and selectivity and high surface area support for the active phase or the metal. They should all fulfill the important properties for tar removal as described above.

**Nickel based catalyst:** Nickel based catalysts are very effective in tar removal process and there are various commercial catalyst available that guarantees tar removal of more than 99%, while increasing the hydrogen content in the syngas with decreasing the light hydrocarbons. These nickel-based commercial catalysts are well studied and experimented by various researchers and found promising tar removal efficiency. Overall, the optimum temperature at which tars get eliminated with nickel based catalyst is at 900°C while increasing the CO and H<sub>2</sub> content in the syngas and it eliminates waste disposal issue [33]. However, presence of sulfur and high concentration of tar content in the syngas to be treated deactivates these nickel based catalyst and needs pre-treatment before the syngas is exposed to the catalyst to avoid deactivation. Moreover, the costs involved in nickel-based catalyst are quite high. Table 9 below summarizes primary possible components of nickel-based catalysts [61].

**Table 9: Composition summary of catalysts**

CATALYST		
Active	Promoter	Support
Ni	Mo	γ- Al <sub>2</sub> O <sub>3</sub>
NiO	CeO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
	Ce-ZrO <sub>2</sub>	SiO <sub>2</sub>
	MgO	Dolomite (CaMg (CO <sub>3</sub> ) <sub>2</sub> )
	Al	Zr O <sub>2</sub>
	Mg	TiO <sub>2</sub>
	WO <sub>3</sub>	CeO <sub>2</sub>
		MgO
		Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub>
		Olivine
		Zeolite
	SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	

It can be seen that natural support such as Dolomite or Olivine can be used in nickel based catalysts. Dolomite is a calcium magnesium ore with the general chemical formula CaMg (CO<sub>3</sub>)<sub>2</sub> and contains on average 20% MgO, 30% CaO and 45% CO<sub>2</sub> on a weight basis [62]. Dolomites are processed through calcinations process at 800-900°C in order to use in tar cracking, which the calcinations involves decomposition of the carbonate minerals, hence removing the CO<sub>2</sub> to form MgO-CaO. Olivine is an alternative to dolomite and is a naturally

occurring mineral which contains Magnesium, Iron oxide and silica. Efficiency of Olivine in tar removal is comparable to that for Dolomite and it can withstand friction, which is not the case for dolomite. Nickel-based commercially available catalysts are summarized below on table 10 [61]:

**Table 10: Summary of nickel-based catalyst in syngas tar removal**

Catalyst	NiO content (wt%)	Support	Reactor temperature range	Tar conversion %
<b>Heavy tar reforming</b>				
BASF G1-25/1	25	CaO–Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub> –K <sub>2</sub> O	785–850	89–99
BASF G1-50	20		660–800	89–99
Haldor Topsoe R-67	15	MgO–CaO–Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub> –K <sub>2</sub> O	780–840	95–100
ICI Katalco 46-1	22		700–875	73–100
Sud Chemie C11-NK	20-25	MgAl <sub>2</sub> O <sub>4</sub> –SiO <sub>2</sub> –K <sub>2</sub> O	600–900	-
		MgO–CaO–Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub> –K <sub>2</sub> O		
		MgO–CaO–SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>		
<b>Light tar reforming</b>				
BASF G1-255	12-15	-	785	88-97
BASF V1693	10,2		850-900	-
Haldor Topsoe RKS-1	15	-	785-800	92
Haldor Topsoe R-67-7H	16-18	MgAl <sub>2</sub> O <sub>4</sub> –SiO <sub>2</sub> –K <sub>2</sub> O	690-780	99
ICI Katalco 57-3	12		-	69
Sud Chemie G-90LDP	14	MgAl <sub>2</sub> O <sub>4</sub>	850-900	99
Sud Chemie G-90EW	14		850-900	99
Sud Chemie G-90B	14	CaO–Al <sub>2</sub> O <sub>3</sub> –SiO <sub>2</sub>	650-900	99
United catalyst C11	10-15	CaO–Al <sub>2</sub> O <sub>3</sub>	725-800	-
		CaO–Al <sub>2</sub> O <sub>3</sub>		
		CaO–Al <sub>2</sub> O <sub>3</sub>		
		Al <sub>2</sub> O <sub>3</sub>		

Since Nickel-based catalyst suffers from deactivation issue due to its usage right after the gasifier for syngas containing large amount of tar. Dolomite or Olivine not only used as support material, but they can be coupled with Nickel based catalyst in separate unit in dual tar removal system, where dolomite or olivine acts are filterer to reduce the tar content before it gets sent to nickel-based catalyst for further tar removal.

**Non-Nickel based catalyst :** Non-Nickel catalysts, such as Rh, Ru, Pd and Pt are studied for tar removal from biomass gasified syngas. Several literatures report that tar in the syngas can



be removed or reduced significantly with help of non-nickel based catalysts into fuel gas. However, these types of catalysts are more costly than the conventional and the nickel based catalysts. Studies conclude that Rh in particular within the non-nickel based catalysts are the most effective component. There are many literature researches available where Rh is tested with various promoter and support materials. According to Asadullah et al, tar removal of 100% was achieved with Rh as active metal with CeO<sub>2</sub> as promoter and SiO<sub>2</sub> as support at 550-700°C. Possible non-nickel metal, promoter and support materials are summarized below on table 11 [63]:

**Table 11: Summary of non-nickel based catalysts in syngas tar removal**

CATALYST		
Active	Promoter	Support
Rh	CeO <sub>2</sub>	SiO <sub>2</sub>
Zn(G-72D)	LaCoO <sub>3</sub>	CeO <sub>2</sub>
Co <sub>3</sub> O <sub>4</sub> (C49-TRX)	Mo <sub>3</sub> O	Al <sub>2</sub> O <sub>3</sub>
Pt, Ru, Pd	Mo	Al(OH) <sub>3</sub>
FeO		ZrO <sub>2</sub>
Fe <sub>2</sub> O <sub>4</sub>		γ- Al <sub>2</sub> O <sub>3</sub>
Fe <sub>3</sub> O <sub>4</sub>		SiAl
MoO <sub>3</sub>		CeO <sub>2</sub> -SiO <sub>2</sub>
CeO <sub>2</sub>		ZrO <sub>2</sub> -SiO <sub>2</sub>
MoO <sub>3</sub> -CeO <sub>2</sub>		CeO <sub>2</sub> -ZrO <sub>2</sub>
Fe(NO <sub>3</sub> ) <sub>3</sub> *9H <sub>2</sub> O		
LaNiO <sub>3</sub>		

**Alkali metal catalyst:** Many researches have been conducted within alkali metal catalyst for tar removal/reforming. However, the studies were for the purpose of adding the catalyst directly into the biomass gasifier to improve the yield and their compositions. Majority of the literature indicates positive composition change; however Sutton et al described such event not cost effective gasification process due to complexity of recovering the catalyst and due to increased ash formation, hence disposing costs [64].

**Basic catalyst:** Alkaline earth metal oxides (MgO, CaO), Natural ores (dolomite, Olivine) and clay minerals belong to the basic catalyst classification. Activities of the basic catalysts are increased by increasing Ca/Mg ratio, active metal content (iron) and decreasing the grain size [65]. Catalytic activity of calcined dolomite versus un-calcined dolomite as downstream catalyst were investigated in terms of tar reduction and it is found that calcined dolomite is better tar reformer due to increased internal surface area and oxygen content on the surface. This conclusion was proven by Hu Et al, where calcined dolomites versus un-calcined dolomite were investigated along with olivine [66].

Natural olivine works as good tar reducing agent, improves the syngas quality and does not tend to form coke. Calcinations of olivine also improve the catalytic activity of the olivine for tar removal. Increase of calcinations duration period found to affect its activity, meaning longer Calcinations period, better catalyst activity in tar reduction in the syngas [67]

**Acid catalyst:** Zeolite, Silica-Alumina belongs to the acid catalysts. Zeolites are solid catalyst and have been widely used in industrial applications since its availability due to its well-defined pore structure, high adsorption capacity, high surface area and due to acidic surfaces. Acidic properties are dependent on original preparation method, form, dehydration temperature and the Si/Al ratio [68]. Modifying the acidic zeolites with dispersed metals offers opportunity to use it in hydrogenation, ring breaking reactions of aromatic hydrocarbons (benzene, toluene, naphthalene, polycyclic aromatics). The advantage of these catalysts in the syngas cleaning application is the high tolerance for sulfur compounds.

For tar reduction, many researchers tested the commercially available zeolite catalysts. For example, Dou et al tested Y-Zeolite, silica, alumina, lime, NiMo for catalytic tar cracking from high temperature fuel gas. The result showed Y-Zeolites and NiMo were the most effective catalyst amongst them. The test run over 10 hours and almost 100% tar removal were achieved and no catalyst deactivation was observed. For the other catalysts, immediate deactivations were observed. Through many research on acid catalyst in tar reforming, it was found in general that acid catalysts have better thermal/hydrothermal stability, resistance towards nitrogen and sulfur due to their acidic properties. Moreover, low cost to obtain and extensive knowledge about the acid catalyst makes it appealing. However, the problem is the fact that rapid catalyst deactivation occurs due to coke formation [69-71].

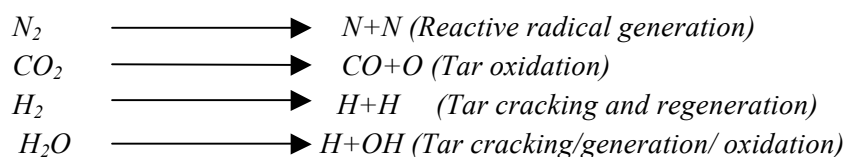
**PLASMA:** Plasma is the fourth state of matter and it contains free radical, ions and excited molecules and they create a highly reactive atmosphere as these reactive species carry enough energy to initiate the tar decomposition reactions [72]. Based on the relative temperatures of the electrons, ions and neutrals, plasmas are divided into thermal and non-thermal plasmas

**Thermal plasma** is in thermal equilibrium with the carrier gas species and electrons at the same temperature. Thermal plasma provides a high temperature environment, much higher than that of the requirement in the gasifier, such that the tar cracking occurs.

**Non-thermal plasmas** have the ions and neutrals at a much lower temperature, while the electron temperature is at significantly higher temperature. Therefore, collision between high energy electron and molecules create the non-thermal plasmas. There are several types of non-thermal plasmas available, namely pulsed corona, dielectric barrier discharges, DC corona discharges, RF plasma and microwave plasmas. Non-thermal plasmas are already successfully utilized in air pollution control for the VOC removal [73-74]. In regards to plasma based tar reforming, Energy Research Centre of The Netherlands (ECN) performed a study of tar reforming by gliding arc plasmas. Gliding arc plasmas belong in between thermal and non-thermal plasmas. However, the result of the study showed only 40% tar removal and such type plasma did not show any selectivity towards hydrocarbons and no difference in selectivity even at higher temperature were observed [55]. Such insufficient tar removals were found to be due to limited radical production as the energy levels of the electrons were too low. Within the non-thermal plasmas, the pulsed corona discharge plasma is found to be the most appropriate for tar reforming. In the actual tar reforming process, use of the generated reactive radicals are core of the process and these reactive radical utilization pathways are dependent

on the process condition, electron/molecule energies (carrier gas) and collision cross section. The most efficient and effective radical utilization pathways were determined through the tar removal/reforming study by means of pulsed corona discharge method, which were conducted by the technical university of Eindhoven in The Netherlands (TU/e). The study involved naphthalene as tar model and various syngas compositions were tested to study their impact on tar removal process. Followings were found to be the optimum process conditions that ensure most efficient reactive radical utilization [75]:

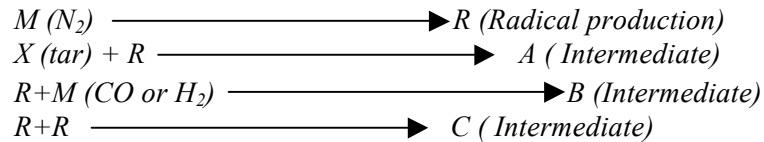
- Tar removal (>95%) at 400°C allows most efficient reactive radicals utilization, hence the temperature at which least amount of energy (225 J/L) is required to carry out the tar removal process.
- Excited nitrogen molecules from the supplied nitrogen gas (N<sub>2</sub>-high energy electron) plays major role in tar cracking. Presence of syngas components (CO, CO<sub>2</sub>, and H<sub>2</sub>) influences the excited nitrogen molecule tar cracking. Oxidation of cracked tars dominate when CO<sub>2</sub> is present syngas, which dissociation of CO<sub>2</sub> (dry reforming) by excited nitrogen molecules enables tar oxidation by the oxygen radicals. Alternatives to (N<sub>2</sub>+ CO<sub>2</sub>), such as N<sub>2</sub>+H<sub>2</sub>O and N<sub>2</sub>+H<sub>2</sub> were also studied, which the N<sub>2</sub>+CO<sub>2</sub> were determined to be suitable option for tar reforming. For N<sub>2</sub>+H<sub>2</sub> case, the reaction rate of H+H+Radical is extremely fast that it takes place even before hydrogen radical initiating the tar decomposition. Therefore, such combination is not favored. The primary radical generation thus can be summarized as below:



- In order to allow N<sub>2</sub> gas to form reactive radicals, the amount of available O<sub>2</sub> should not exceed 3.6%. The study had also determined, more amount of N<sub>2</sub> present, more reactive radicals are formed. Thus, the plasma system must be at least fed with 50% of N<sub>2</sub>.
- Efficient utilization of generated oxygen radicals is controlled by process condition, such that the tar reforming is not terminated by presence of CO, H<sub>2</sub> and CH<sub>4</sub>. Because, presence of CO and H<sub>2</sub> do affect the tar reforming process of N<sub>2</sub>+CO<sub>2</sub>, as it reacts with oxygen radicals to generate CO<sub>2</sub> and H<sub>2</sub>O. Dissociating the CO<sub>2</sub> further requires more energy and water presence in the syngas gets increased. The amount of water formed as a result of tar cracking oxidation termination by hydrogen cannot be quantified due to lack of literature. Therefore, these reactions should be avoided as much as possible by means of process condition.
- Although, 400°C were determined to be optimum energy efficient temperature, there will be usage of the oxygen radicals by the CO and H<sub>2</sub> in the syngas. Reaction rate constant for O+H<sub>2</sub> is higher than that for O+CO. Therefore, water in the syngas will be increased and termination of tar oxidation will be dominated by H<sub>2</sub> in the syngas. At higher than 400°C, the rate constant for both (CO+H) continues to increase and energy requirement increases drastically.
- In contrast, at 200°C, tar oxidation termination by H<sub>2</sub> will not be present, but will be terminated by CO. However, at this temperature, it requires twice as much (400-500 J/l) of energy than that for at 400°C.

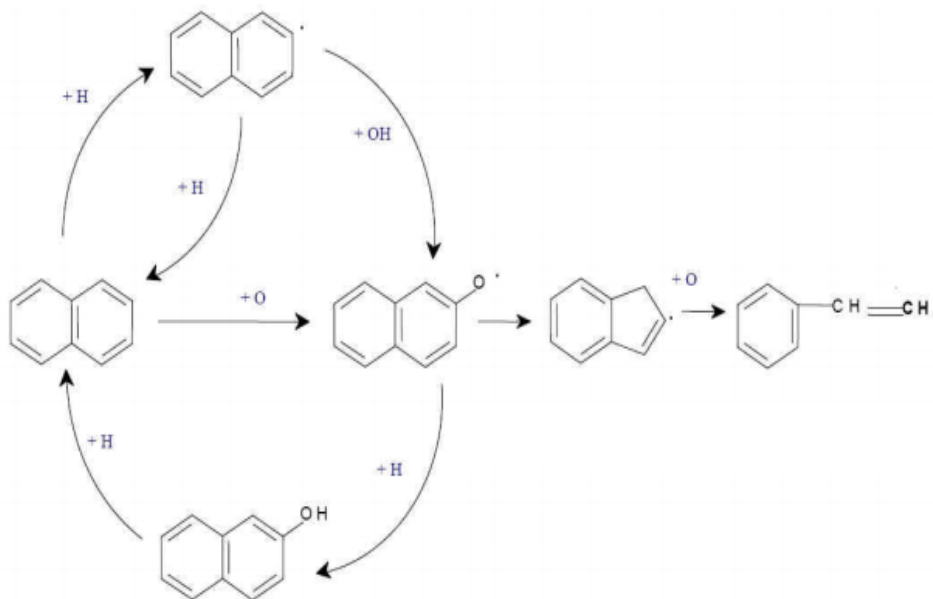
- Low pressure is preferred for syngas tar cracking, as it reduces the density of the syngas components (CO, H), which their effect for radical termination will be less.
- Presence of CH<sub>4</sub> component in the syngas were studied, which the model syngas had 1% of methane and had concluded no effect on tar oxidation termination. No details on high methane concentration, as it are in case in fixed bed gasifier syngas containing higher than 1% of methane were found.

Therefore, above described tar cracking and useful oxygen radical utilization by syngas components can be summarized by followings:



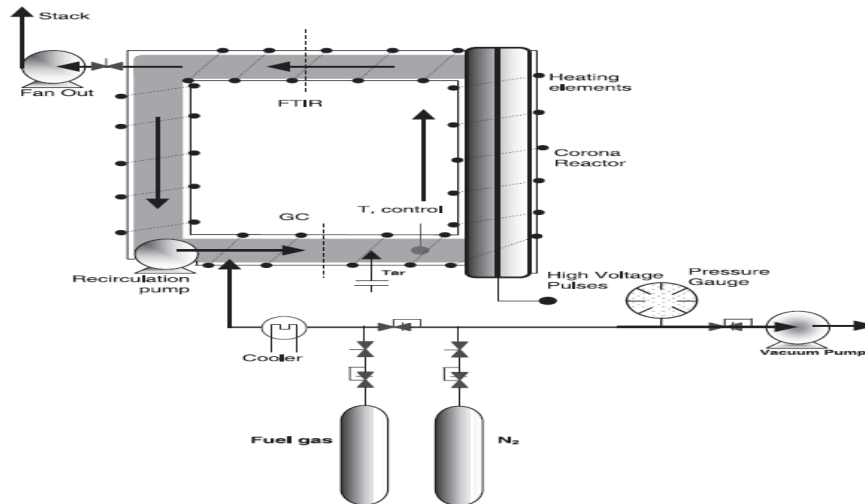
In ideal situation, formation of intermediates B, C should be avoided, such that generated radicals by the background gas (N<sub>2</sub>) is only utilized to form intermediate A. For such reaction to dominate in the process, the energy density against tar removed plot should give linear relation. If the relation is exponential in nature, it is an indication that linear termination by the CO, H<sub>2</sub> termination reactions are dominant. Polynomial relation is an indication that radical radical termination is dominant. Hence linear relation should be desired.

Consequently, the mechanism involves oxidation through O radicals sourced from CO<sub>2</sub> dissociation and the hydrogen acts as the main terminating component for the oxygen radicals. Such reaction mechanisms were confirmed by other studies conducted with pulsed corona discharge plasma. Figure 10 below shows scheme for the decomposition of naphthalene:



**Figure 10: Naphthalene decomposition scheme [75]**

The tar components were measured with help of both FTIR (Bruker, model VECTOR 22) and a GC (HP5890). The GC is equipped with a FID and a Chrompack CP-Sil 5 CB fused silica wall coated open tubular (WCOT) column to measure the heavy hydrocarbons. The experimental set up of this study is shown below on figure 11:



**Figure 11: Experimental set up [75]**

Although, there are various lab scaled pulsed corona discharge reactors available, there is none at commercial scale as this technology is not mature. In addition, the energy needed for the plasma process is often debated and is one of the main reasons why the plasma method is still commercially not available. The above mentioned study had found that the energy needed for plasma process decreased with increasing the temperature up to 500°C. However, the study had concluded the optimum plasma temperature from the kinetic model and the experimental results are at 400°C and at this temperature the energy consumption is in range of 200-250 J/L of syngas to be treated. Therefore, the present state of technology development requires 20% of the final electrical output from the gasified syngas (biomass) for the tar removal process. It is believed that reducing the energy demand down to 5% would help to realize a complete system for industrial purpose. Table 12 below summarizes the used of pulsed corona discharge plasma applications:

**Table 12: Pulsed corona discharge plasma utilization applications for pollution control and sustainable development [76]**

Applications	Role	Maturity
<b>Indoor</b>	Bacterial, virus and odor removal	Mature
	Converting NO <sub>x</sub> and SO <sub>2</sub> to NH <sub>4</sub> NO <sub>3</sub> and (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> under NH <sub>3</sub> addition	Industrial demonstration
	To remove gaseous, heavy metals and particles simultaneously	Industrial demonstration
	NO <sub>x</sub> reduction	Concept proof
	Dioxin, Furans and Hg removal	Industrial demonstration
<b>Air cleaning</b>	Odour, VOCs and micro-organisms removal	Close to mature
<b>Syngas cleaning</b>	Tar reforming, CO to CO <sub>2</sub> conversion, gaseous and heavy metals removal	Industrial demonstration
<b>Methane reforming</b>	Converting methane to higher hydrocarbons	Concept proof
<b>Oil reforming</b>	Upgrading heavy oils to light oils	
<b>Soil cleaning</b>	Organic pollutants and micro-organisms removal	Concept proof
<b>Soil cleaning</b>	Organic pollutants and micro-organisms removal	Concept proof
<b>Water cleaning</b>	Organic pollutants and micro-organisms removal	Demonstration

**WATER-BASED-GAS-SCRUBBING:** Water based syngas tar removal technology has been in operation since 2000 at the Harboore updraft gasification plant in Denmark [77]. The technology is licensed to Japanese company JFE and German company Relax Umwelttechnik. The principle of the technology involves cooling of the syngas through series of district heating shell and tube heat exchangers, where large amount of water and tars get separated. Then the gas is further treated to remove remainder water/tar aerosols and dust in a wet ESP. However, such technology result large amount of tar contaminated water and additional steps needed to treat the water [48].

**OIL-BASED-GAS-SCRUBBING (OLGA):** OLGA technology employs multi-stage scrubber containing special oil and is developed by ECN and Dahlman. This technology not only removes the tars efficiently, it also removes the dust, thiophenes and dioxins. The technology is originally designed to remove tars from syngas resulted from gasifier operating high temperature (800-900°C). The main principle of OLGA technology is about controlling the tar dew point before it becomes problematic. It involves cooling of the syngas down to or close to inlet of OLGA process temperature (just above tar dew point of the gas). Then the actual tar separation process starts by condensing the heavy tars by cooling the gas from just above the tar dew point to just above the water dew point, followed by light tars removal in the adsorption column. As a result, the conventional water-based scrubbing technologies can be applied without mixing the water with tars. Controlling of the tar dew point principle is demonstrated below on figure 12 [78]:

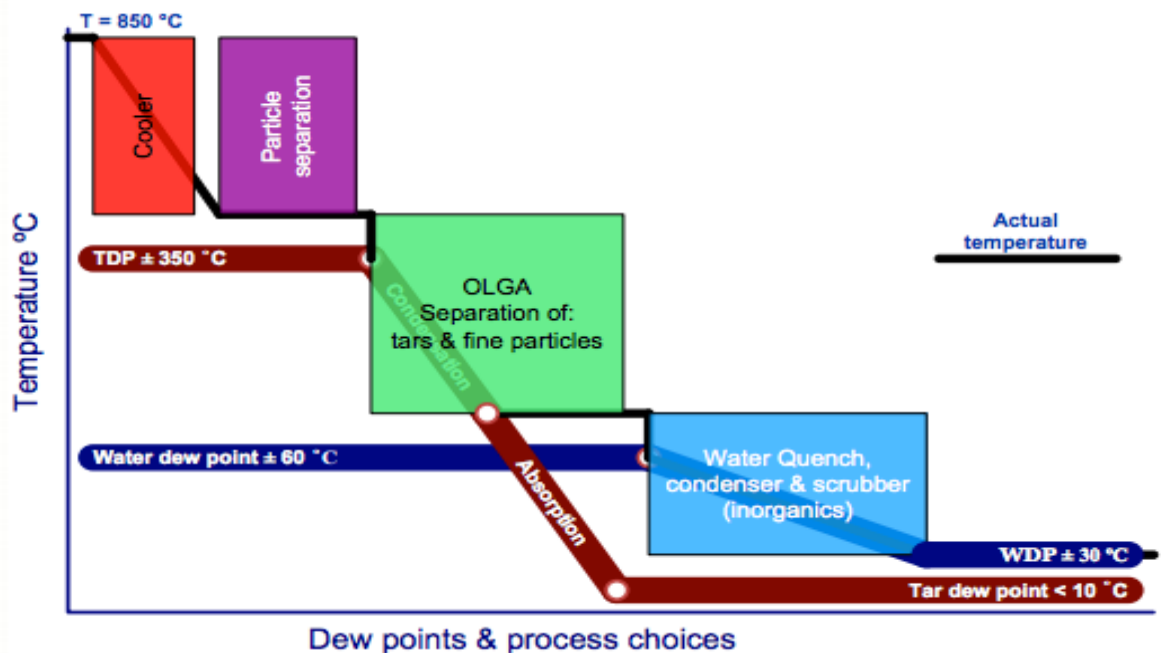


Figure 12: Tar dew point control principle in OLGA technology [78]

The first stage would be cooling of the syngas in the collector containing special oil and there the heavy tars start to condense and condensed tar is collected and removed from the collector scrubber and sent to the gasifier that the OLGA technology is coupled with. The second stage employs absorber and stripper where it takes care of the light tars. The light tars get removed in the absorber containing the scrubbing oil and gas leaving the absorber column should be free of tars. The scrubbing oil in the absorber column will be saturated with light tars and they are regenerated in the stripper unit where hot air is used to strip the light tars off the scrubbing oil and the hot air containing light tar is designed to feed to the gasifier. The working principle of OLGA technology is shown below on figure 13:

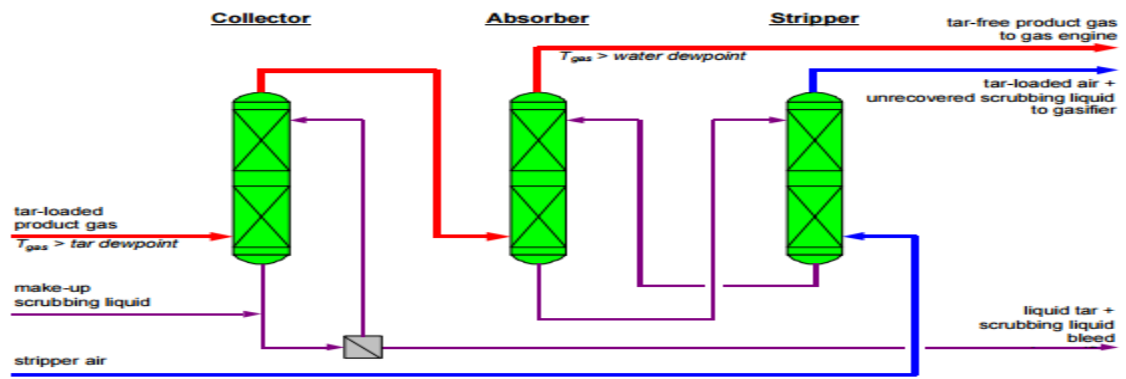


Figure 13: Working principles of OLGA technology [78]

Use of OLGA technology for low temperature gasification will need some modification as it is originally designed for high temperature gasifiers. This is because the syngas composition and tars in the syngas from low temperature gasifier are different than that from high temperature gasifiers. Modification to low temperature gasifiers were tested at lab scale, but there are none operating at pilot/demonstration/commercial scale. Table 13 below shows where OLGA technologies are currently under operation:

Table 13: OLGA technology references

	Project	Location	Year of installation
1	0,8 MWth pilot plant at ECN facility	Petten, The Netherlands	NA
2	7 MWe plant with RDF, SRF and local wood as feed	United kingdom	
3	Chicken manure gasification	Tondela, Portugal	2010
4	1 MWe CHP project on soy residue-Thermax	Washim, India	2014
5	4 MWe CHP-In operation in 2015	India	2014
6	Commercial scale of OLGA system (2000 m <sup>3</sup> /hr)	Moissannes, France	NA

Therefore, Core of such technology is use of the scrubbing oil, which the properties of this oil are unknown as the technology patent belongs to ECN. Through literature research, it was found quite a few investigations were conducted at lab scale to determine what type of oil best suits the separation of tars, which glycerol, biodiesel fuel, diesel fuel, vegetable oil, bio-oil as by product of biomass gasification were tested. According to the literature, it was found that the biodiesel fuel had the best tar removal efficiency. However, due to diesel fuel's fast evaporation properties, it leads to formation of Gravimetric tars. Biomass gasification plant in Gussing, Austria (Biomass Power Plant Güssing Ltd) uses bio-diesel as scrubbing oil to remove the tar [79-80].



**4. GAS CLEANING TECHNOLOGY SELECTION**

In the literature review of gasification process and gasifier types, it was found that the fixed-bed gasifier gives the highest amount of tar in the syngas due to the gasifier type and its operating conditions. Moreover, formation of tar gets significant in the case where small-scaled fixed-bed gasifiers are used to produce fuel gas. Use of small-scaled fixed-bed gasifier is common practice amongst developing countries for fuel gas generation. The commercially available tar removing technologies originally designed for large scaled gasification plants are not suitable for small-scaled gasifiers due to economic and technical constraints. Lack of syngas cleaning technologies for small-scaled fixed-bed gasifiers gives no option, but to use expensive coal to generate fuel gas to minimize syngas cleaning requirement. Therefore, use of expensive coal is better for small-scaled fixed-bed gasifiers, as it gives almost no tar or little tar containing syngas. This leads to no need or little syngas tar removal cleaning. Throughout the literature review on syngas cleaning technologies as summarized on table 7 above, it was found that the plasma methods to remove tar had potential. The literature research had shown that the plasma methods were successfully tested for biomass based tar removal and had given promising results. On the other hand, there are no publicly available literatures focusing on coal based tar removal by means of the plasma method. This has lead to interest of testing compatibility of plasma based cleaning method, in particular the non-thermal pulsed corona discharge plasma for coal based tar reforming. Although, there are differences between coal and biomass tars, compatibility of non-thermal plasma method were predicted to be suitable for coal tar removal due to non-thermal plasma’s operating nature. Coal tar is generally much more aromatic than biomass tar; meaning coal tar has lower H/C and O/C ratios.

The compatibility of non-thermal pulsed corona discharge plasma was tested by integrating the plasma unit with fixed-bed gasifiers of two different sizes. The integrations of the gasifiers with plasma unit were simulated with help of Aspen Plus V7.3. Tar free syngas exiting the pulsed corona discharge plasma reactor were further assessed and their matching applications were determined. The simulation work and the application matching process can be found in the following sections:

**4.1. CASES**

In order to assess the feasibility of pulsed corona discharge plasma unit for coal syngas tar cleaning, their assessments are done by applying them to below described cases, which will be referred as ‘‘Small case (1500 kg/hr daf)’’ and ‘‘Large case (26400 kg/hr daf)’’. The analyses of coal samples are often performed on air-dried samples and then the constituents are reported on air-dried basis. Coal analytical results can also be reported on different bases, such as As-received (ar), Air-dried (ad), Water-Free (wf), Water and Ash-Free (daf) and Dry mineral matter-Free (dmmf). Coal analytical results in different bases are done by appropriate correlations. The relationship of different analytical basis to various coal components are shown below on figure 14:

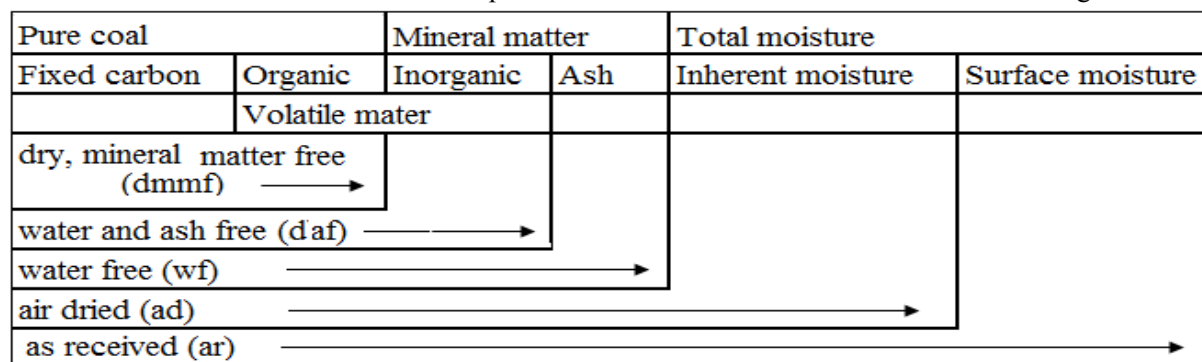


Figure 14: Coal analytical result reporting different basis [15]



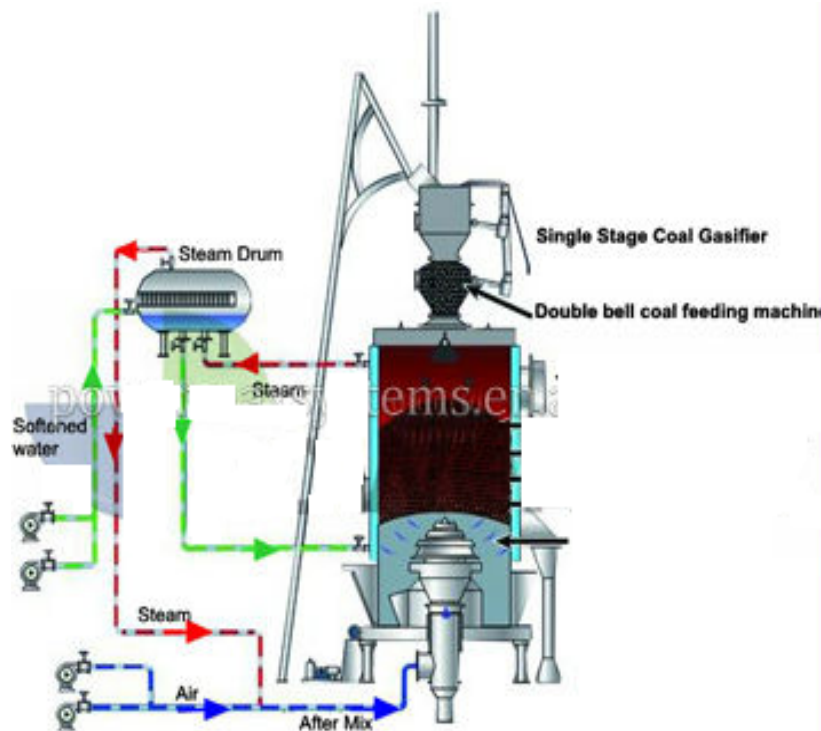
In both cases the feed coal is in daf (dry ash free coal) state. This is a method of expressing the coal analytical result based on hypothetical conditions, which the coal is free from both moisture and ash [80]. Apart from the difference in fed coal amounts, the small case uses ambient fixed-bed gasifier, while the large case utilizes fixed-bed gasifier operating at 30 bars.

**4.1.1. SMALL CASE**

For this case ambient fixed-bed gasifier is utilized to generate the syngas to be cleaned from the fed feedstock. The structural chart of such gasifier is shown below on figure 15:

*Table 14: Gasifier specification [82]*

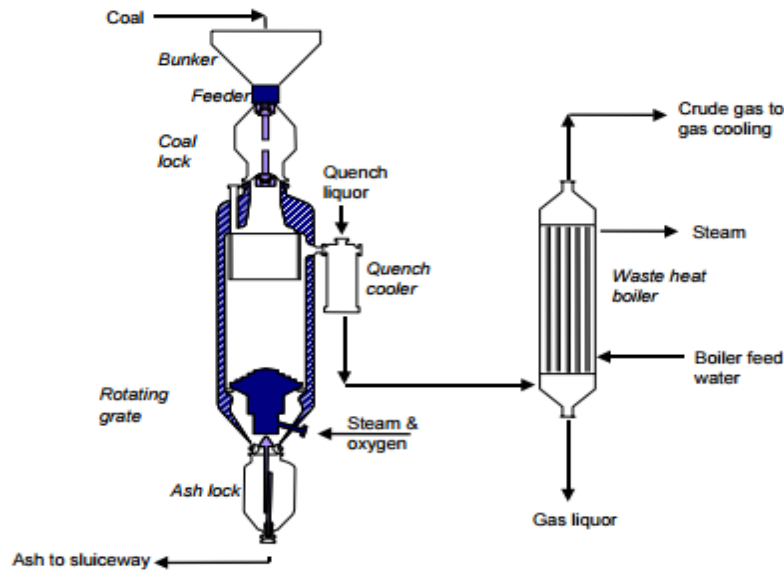
Inner diameter of furnace (mm)	2600
Sectional area of furnace (m <sup>2</sup> )	5.31
Applicable coal	Non-caking or weak caking anthracite or coke
Coal size (mm)	13-100
Coal consumption (kg/h)	1000-1500
Gasifying agent	Air+Steam
Air consumption (m <sup>3</sup> /kg coal)	2.0-2.5
Steam consumption (m <sup>3</sup> /kg coal)	0.25-0.40
Syngas output (Nm <sup>3</sup> /hr)	3000-4600
Syngas output pressure (Kpa)	<1.5
Syngas output temperature (°C)	400-500



*Figure 15: Structural chart of the ambient fixed- bed gasifier [82]*

**4.1.2. LARGE CASE**

The large case utilizes fixed-bed gasifier at high pressure to generate syngas. The gasification process is sui for a large variety of coal feedstock. The feedstock is gasified at a typical pressure of 30 bars in the presence of steam and oxygen (air) as gasification agents. The feed for this case 26400 kg/hr of dry ash free coal and the sketch of the gasifier is shown below on figure 16:



**Figure 16: High-pressure fixed-bed gasifier [83]**

For this research work, Aspen plus V7.03 were utilized to simulate the fixed-bed gasifier using the Gibbs reactor. The syngas exiting the gasifiers are fixed at followings and following values come from Air-Liquide’s operating experience in fixed-bed gasifiers:

- Steam/Oxygen (air) ratio at 0.8. At this ratio, enough steam is fed to the gasifier to keep the ash temperature lower than the ash melting temperature.
- Keeping steam to oxygen ratio at 0.8 and supplying enough oxygen and steam to gasify all the carbon in the fed coal.
- Methane
  - Small scaled atmospheric gasifier:  $100 \text{ m}^3/\text{t}_{\text{daf-lignite coal}}$
  - Small scaled atmospheric gasifier:  $30 \text{ m}^3/\text{t}_{\text{daf-coke}}$
  - Large scaled 30 bar gasifier:  $200 \text{ m}^3/\text{t}_{\text{daf-lignite coal}}$
  - Large scaled 30 bar gasifier:  $100 \text{ m}^3/\text{t}_{\text{daf-coke}}$
- Shift reaction, such that CO and CO<sub>2</sub> are in 1 to 1 ratio respectively
- All the organic sulphur gets out as part of syngas, which 90% of them in H<sub>2</sub>S and 10% in COS forms – The same trend applies when coal tar gets cracked and forms syngas components.
- 80% of the nitrogen from the feedstock gets converted to NH<sub>3</sub> and 20% gets converted to HCN- The same applies for tar cracking
- 3% of the total available carbon from coal goes into the ash

For both cases, the gasifiers are fed with tar forming low rank coal (requires tar reforming unit) and with non-tar forming good quality coke (does not require tar reforming). The feedstock analysis of the coal and the coke are summarized below on table 15:

**Table 15: Feedstock (Coal and Coal) analysis result summary [84]**

Properties		Unit	COAL	COKE
Total moisture, W <sup>ar</sup>		%	32.68	4.07
Proximate analysis	Ash, A <sup>ad</sup>	%	7.85	16.84
	Volatile matter, V <sup>ad</sup>	%	29.10	0.66
	Fixed carbon, C <sup>ad</sup>	%	33.32	81.89
Sulphur, S <sup>t</sup> <sub>ad</sub>		%	0.16	1.54
Ultimate analysis	C <sup>daf</sup>	%	71.08	96.84
	H <sup>daf</sup>	%	5.10	0.18
	N <sup>daf</sup>	%	1.16	0.97

	O <sup>daf</sup>	%	22.40	0.15
Higher heating values, Q <sup>ad</sup>		kJ/kg	17519	27351
Lower heating value, Q <sup>ad</sup>		kJ/kg	16112	27304
Ash melting behavior	Initial deformation, DT	°C	1190	1300
	Spherical, SDT	°C	1220	1330
	Hemispherical, HDT	°C	1240	1360
	Ash fluid, AFT	°C	1290	1380
Ash composition	Al <sub>2</sub> O <sub>3</sub>	ad, %	16.50	25
	Fe <sub>2</sub> O <sub>3</sub>	ad, %	12.30	8.2
	TiO <sub>2</sub>	ad, %	0.80	0.9
	SiO <sub>2</sub>	ad, %	42.00	46.4
	CaO	ad, %	17.00	8.4
	MgO	ad, %	3.10	2
	K <sub>2</sub> O	ad, %	1.20	1
	P <sub>2</sub> O <sub>5</sub>	ad, %	1.1	0.6
	MnO	ad, %	0.30	0.1
	SO <sub>3</sub>	ad, %	4.70	5.8
	Na <sub>2</sub> O	ad, %	0.60	1.3

When the fixed-bed gasifier is fed with coal with above shown properties, they will produce syngas with tar. The tar yields and their compositions are shown below in table 16:

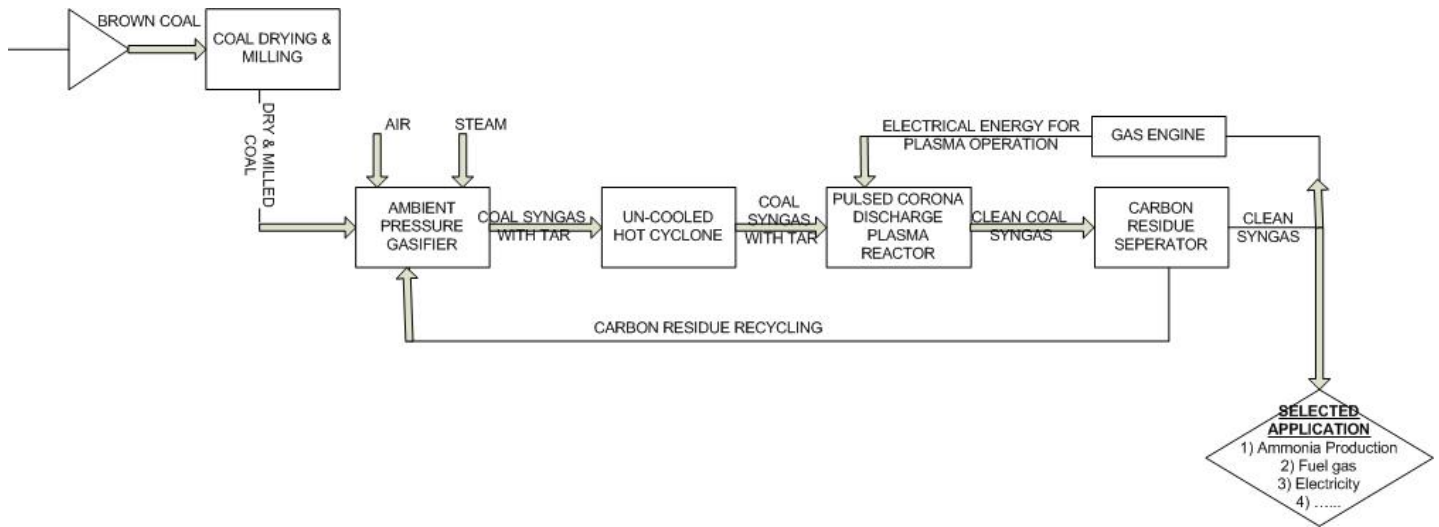
**Table 16: Tar yield from coal gasification [84]**

Tar kg/tdaf-188,03
--------------------

The gasification of the coal gives syngas with tar yield of 188, 03 kg per tdaf coal. The target of this research work is to remove/reform the tar yield. According to the tar definition by ECN, tar, oil and naphtha as a whole are referred as tar throughout the report.

**4.2. PULSED CORONA DISCHARGE PLASMA SIMULATION RESULTS:**

The simplified block-flow-diagram (BFD) with pulsed corona discharge plasma reactor integrated in the process is shown below on figure 17:



**Figure 17: BFD of coal gasification with FBDB-gasifier with pulsed corona discharge plasma reactor integrated**

Consequently, the plasma reactor is located downstream of the fixed-bed gasifier and is fed with coal syngas with tar exiting the gasifier. The exiting syngas from the plasma reactor should be free of tars and small amount of carbon contaminated, which is to be separated in the carbon residue separator before it is sent to its application usages. In the following sections, the results from the simulation for both cases (large and small) are discussed further.

**4.2.1. SMALL CASE-1500 kg/hr (daf) COAL AS FEED**

According to the pulsed-corona-discharge plasma principle, the tar in the syngas gets cracked into smaller hydrocarbons/syngas components, hence improves the heating value of the syngas. To simulate the ambient fixed-bed gasifier for syngas generation, the tar content is deducted from the coal content and remainder (coal without tar) is fed to the gibbs reactor with air and steam as gasifying agents (S/O ratio of 0.8) to get syngas from the gasifier. Then, the syngas together with tar content (expressed in C, O, and H contents) are fed to another gibbs reactor with no gasifying agents supply. This is to mimic the plasma reactor and the syngas exiting the plasma reactor gives details on how much of an additional content in CH<sub>4</sub>, CO and H<sub>2</sub> can be produced from the tar reforming. Such that syngas generation with its maximum content from the feed can be estimated. The operating conditions for the gibbs reactors are at 1 atm and 400°C, as it is the typical operating conditions for small-scaled atmospheric fixed-bed gasifiers and the plasma unit operates at 400°C, which require no need of temperature adjustment for the syngas exiting the gasifier and not having to adjust the temperature to match its downstream unit is a major advantage.

In addition, the simulation for the small-scaled fixed-bed gasifier fed with costly non-tar forming coke type coal is performed. The syngas from such option does not need tar cleaning steps, as it does not produce any or only small amount of light tar. Therefore, the simulation outputs are compared to that from the tar forming coal fed gasifier and cleaned through plasma unit. Hence, it allows to see whether gasifying the coal and reforming the tar is economical compared to gasifying costly coke type coal where no installation of tar reforming or cleaning unit is required. The syngas compositions of such options are shown below on table 17:

**Table 17: Syngas generation simulation results for Coal and Tar and mixed**

Mole Flow kmol/hr	S-Coal <sup>1</sup>	S-Tar+Coal <sup>2</sup>	S-COKE <sup>3</sup>
CARBON (C)	0.00	0.68	0,00
OXYGEN (O)	0.00	0.00	0.00
HYDROGEN (H)	60.48	52.55	62.40
NITROGEN (N <sub>2</sub> )	67.72	67.72	197.26
METHANE (CH <sub>4</sub> )	6.65	18.24	2.00
CARBONMONOXIDE (CO)	31.62	34.52	57.41
CARBONDIOXIDE (CO <sub>2</sub> )	31.59	30.01	57.40
WATER (H <sub>2</sub> O)	4.92	6.50	0.04
SULPHUR (S)	0.00	0.00	0.00
HYDROGEN-SULFIDE (H <sub>2</sub> S)	0.07	0.10	0.72
CARBONYL-SULFIDE (COS)	0.01	0.01	0.08
AMMONIA (NH <sub>3</sub> )	1.86	2.00	1.66
HYDROGEN-CYANIDE (HCN)	0.47	0.47	0.42
<b>Total molar flow</b>	205.38	212.80	379.27
<b>Flow (m<sup>3</sup>/hr)</b>	4603.39	4769.69	8500.96
<b>LHV (MJ/m<sup>3</sup>)</b>	6.28	7.78	3.88
<b>Energy stream (MJ/hr)</b>	<b>28909.29</b>	<b>37108.19</b>	32983.72

	Air (kg/hr)	Steam (kg/hr)
<b>A (Coal)</b>	2473.01	415.46
<b>D (Coke)</b>	7203.90	1210.26

<sup>1</sup>Coal syngas before entering the plasma reactor, still contains the tar (from gasifier)

<sup>2</sup> Coal syngas exiting the plasma reactor, tar >95% reformed

<sup>3</sup> Coke gasified at same condition that for coal

Some components of the syngas exiting the gasifier for both cases (coal or coke fed) are fixed as discusses earlier. It is assumed that all the carbon in the coal syngas gets converted to methane in the plasma unit, which we would expect to see increase in methane content in the syngas exiting the plasma unit. According to non-thermal pulsed corona discharge plasma unit’s operation, the tar is broken down to lighter hydrocarbons ranging from methane up until benzene. Therefore, in reality not all the tars are reformed to methane. However, in order to investigate whether use of non-thermal pulsed corona discharge plasma in coal syngas tar reforming is technologically feasible, it is assumed that all the tar is converted to methane.

To account for the inefficiency of the plasma reactor, 5% of the total carbon atoms available from tar were by-passed, allowing the remainder 95% of the carbon to form methane. The by-passed 5% of the total available carbon atom in the tar will be converted to a solid carbon residue, which is to be separated from the syngas and will be a loss. In order to convert the 95% of the free carbon atoms from the tar, the syngas exiting the plasma reactor should at least contain 18.24 kmol/hr of methane. It was seen that for the fed amount of coal, there were 221 kg/hr of tar in sub-bituminous coal, which 80% of them were carbon, while the remainder were either oxygen or hydrogen. Therefore, to convert these carbons, the only source of hydrogen was from the coal syngas, which is the reason for reduction in hydrogen amount in the syngas. Therefore, by looking at the syngas components before and after the plasma reactor, followings can be said:

- Total syngas volume increases from 4603.39 m<sup>3</sup> to 4769.69 m<sup>3</sup>

- Methane content in the syngas increased from 6.65 kmol to 18.24 kmol, while hydrogen content decreases from 60.48 to 52.55 kmol. This is the maximum amount of methane that can be produced as a result of tar reforming under assumption that supplied electricity to the plasma is enough to reform the tars into lighter hydrocarbons, which lighter hydrocarbons are 100% methane.
- Syngas heating value increases from 6.28 to 7.78 MJ/m<sup>3</sup>, hence, hourly energy stream (MJ/hr) is increased by approximately 20%. However, when the overall energy balance is looked at, it will be less than 20%. Because to support the plasma operation, certain amount of syngas will need to be used to generate electricity. However, plasma energy demand source will be decided later on after making economical analysis, as the costs of supplying the energy to the plasma will impact the economic.
- Comparing the coke syngas with coal-tar-reformed syngas, it can be seen that total energy stream of tar reformed syngas is higher than that from the coke syngas, although there is volume difference. However, the lack of volume in the sub-bituminous coal syngas case is offsetted by the higher low heating value of the syngas due to tar reforming.
- Gasifying low rank sub-bituminous coal and reforming the tar with help of plasma unit gives syngas with higher energy stream than that from the expensive coke gasified case. However, due to composition differences, their usage applications will vary

#### 4.2.2. LARGE CASE-26400 kg/hr (daf) COAL AS FEED

The large case utilizes the high pressure fixed-bed gasifier to generate the syngas. For this case, exactly the same conditions that for the small case is used, except the gasifier pressure is increased to 30 bars. Therefore, methane formations for L-Coal and L-Coke are altered due to high pressure:

**Table 18: Syngas generation simulation result for Coal and Tar and mixed**

Mole Flow kmol/hr	L-Coal <sup>1</sup>	L-Tar+Coal <sup>2</sup>	L-COKE <sup>3</sup>
CARBON (C)	0.00	12.23	0.00
OXYGEN (O)	0.00	0.00	0.00
HYDROGEN (H)	785.68	645.83	1160.92
NITROGEN (N <sub>2</sub> )	1020.00	1020.00	3521.44
METHANE (CH <sub>4</sub> )	235.57	444.01	11.78
CARBONMONOXIDE (CO)	513.67	563.18	1023.85
CARBONDIOXIDE (CO <sub>2</sub> )	513.36	487.69	1023.86
WATER (H <sub>2</sub> O)	64.53	90.19	0.8
SULPHUR (S)	0.00	0.00	0.00
HYDROGEN-SULFIDE (H <sub>2</sub> S)	1.16	1.76	13.78
CARBONYL-SULFIDE (COS)	0.13	0.13	1.53
AMMONIA (NH <sub>3</sub> )	32.91	35.50	14.63
HYDROGEN-CYANIDE (HCN)	8.23	8.23	3.66
<b>Total molar flow</b>	3175.24	3308.75	6776.25
<b>Flow (m<sup>3</sup>/hr)</b>	71169.83	74162.28	151882.87
<b>LHV (MJ/m<sup>3</sup>)</b>	7.37	9.44	3.81
<b>Energy stream (MJ/hr)</b>	524521.65	700091.92	578673.73

	Air (kg/hr)	Steam (kg/hr)
<b>A (Coal)</b>	37250	6258
<b>D (Coke)</b>	128601.30	21605.02

<sup>1</sup>Coal syngas before entering the plasma reactor, still contains the tar (from gasifier)

<sup>2</sup> Coal syngas exiting the plasma reactor, tar >95% reformed

<sup>3</sup> Coke gasified at same condition that for brown coal

The trends observed in the small case in regards to syngas composition are seen for the large case before and after reforming (decrease of syngas volume, hydrogen and significant/slight increase of methane and CO components respectively). It can be further seen that, increase of gasifier pressure results increased low heating value of the syngas compared to the small cases.

#### 4.2.3. ENERGY CONSUMPTION FOR PLASMA REACTOR

For the cases where coal is utilized, it will need plasma to reform the tar content. According to S.A.Nair et al [76], it requires 225 J/L (225 000 J/m<sup>3</sup>) of energy. Such energy densities are translated into above cases and are summarized below in terms of MWh and syngas.

**Table 19: Energy consumption of plasma unit**

	<b>SMALL-COAL-PLASMA</b>
<b>Syngas-Plasma-in (kmol/hr)</b>	<b>236.82</b>
<b>Syngas-Plasma-in (m3/hr)</b>	5308.08
<b>Energy density (MW/hr)</b>	<b>0.37</b>
Syngas (m3/hr)	<b>448</b>
Total Syngas (m3/hr)	<b>4769.69</b>
<b>% of the syngas</b>	<b>9.40</b>

\*Gas engine with 38% efficiency is taken into account in order to convert syngas to 0, 37 MW electricity.

For the small case, it needs 9.4% of the total cleaned syngas from the plasma reactor to generate 0.37 MW electricity using gas engine with 38% efficiency [85]. This leaves the remainder 90.6% of the clean syngas available for suitable applications. As a result of employing the plasma method and supplying the energy demand from the cleaned syngas (9,4%), gives net increase of energy stream from 28909.29 MJ/hr (Syngas with tar) to 33620.02 J/hr (clean syngas), which is 14 % increase in energy stream-wise.

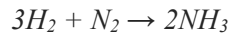
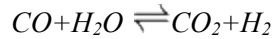


**4.3. APPLICATION MATCHING**

The non-thermal pulsed corona discharge plasma reactor with small-scaled fixed-bed gasifier was simulated and the result showed it is technologically feasible to reform the tars. The clean syngas free of tar is ready to be sent to possible applications and matching applications are determined. As a start, high nitrogen content in the syngas narrows down the possibilities to usage in ammonia production and as fuel gas production for heating or electricity generation. The nitrogen content is sourced from the air gasification agent and one of the criteria for plasma reactor is to have syngas with at least 50% of nitrogen content [76]. Thus, these two applications are considered further. For other applications, the high quantity of nitrogen should be removed before the syngas is utilized further. However, removal of nitrogen contaminants from the syngas by means of distillation is very complex and prohibitively expensive at modest scale. Therefore, due to economic reasons at considered scale, use of nitrogen-contaminated syngas for further application by removing the nitrogen contaminants by cryogenic nitrogen removal is not economically feasible.

**4.3.1. AMMONIA PRODUCTION**

For ammonia production, the total CO content of the syngas should be shifted to increase the hydrogen content in the syngas according to the below first equation, which then hydrogen will react catalytically with nitrogen according to Haber-Bosch process to make ammonia [86]



The table 20 below shows the syngas compositions exiting the plasma reactor from the small case:

*Table 20: Syngas exiting the plasma reactor*

Mole Flow kmol/hr	S-Tar+Coal <sup>2</sup>	%
CARBON (C)	0.68	0.32
OXYGEN (O)	0.00	0.00
HYDROGEN (H)	52.55	24.69
NITROGEN (N <sub>2</sub> )	67.72	31.82
METHANE (CH <sub>4</sub> )	18.24	8.57
CARBONMONOXIDE (CO)	34.52	16.22
CARBONDIOXIDE (CO <sub>2</sub> )	30.01	14.10
WATER (H <sub>2</sub> O)	6.50	3.05
SULPHUR (S)	0.00	0.00
HYDROGEN-SULFIDE (H <sub>2</sub> S)	0.10	0.05
CARBONYL-SULFIDE (COS)	0.01	0.00
AMMONIA (NH <sub>3</sub> )	2.00	0.94
HYDROGEN-CYANIDE (HCN)	0.47	0.22
<b>Total molar flow</b>	212,8	-
<b>Flow (m<sup>3</sup>/hr)</b>	4769.69	-
<b>LHV (MJ/m<sup>3</sup>)</b>	7.78	-
<b>Energy stream (MJ/hr)</b>	<b>37108.2</b>	-

It can be seen from the above table that, one third of the syngas is nitrogen. Converting the available CO through water-gas-shift reaction to form hydrogen provides in total of 87.07 kmol/hr of hydrogen available. For such amount of hydrogen, 29 kmol/hr of Nitrogen is needed to make 58 kmol/hr of Ammonia. Required nitrogen for Haber process [86] is already present in the syngas and it can be seen that the syngas contains lot more (38.70 kmol/hr) nitrogen than it needs in ammonia production. Therefore, it can be concluded from this point

on that the use of clean syngas from plasma reactor cannot be utilized for ammonia production due to its high content of nitrogen.

**4.3.2. FUEL GAS**

The fuel gas is composed of hydrocarbon (methane), hydrogen and carbon monoxide. Fuel gas is source of heat energy that can be transmitted and distributed through pipes from the original source to the destination of the consumption. The table 21 below shows the amount of syngas and their compositions available exiting the plasma reactor (Small case):

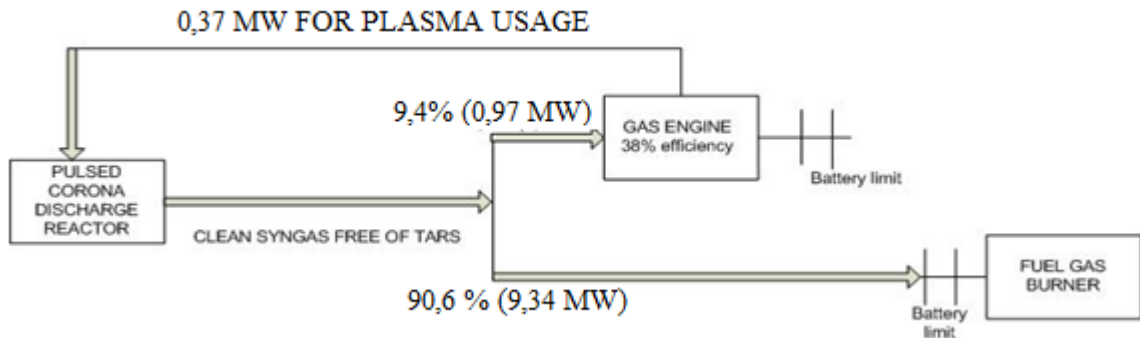
*Table 21: Syngas exiting the plasma reactor*

Mole Flow kmol/hr	S-Tar+Coal
<b>Total molar flow</b>	212.80
<b>Flow (m<sup>3</sup>/hr)</b>	4769.69
<b>LHV (MJ/m<sup>3</sup>)</b>	7.78
<b>Energy stream (MJ/hr)</b>	<b>37108.19</b>

For the fuel gas application, following 2 cases are considered:

**4.3.2.1. Case 1: Direct burning**

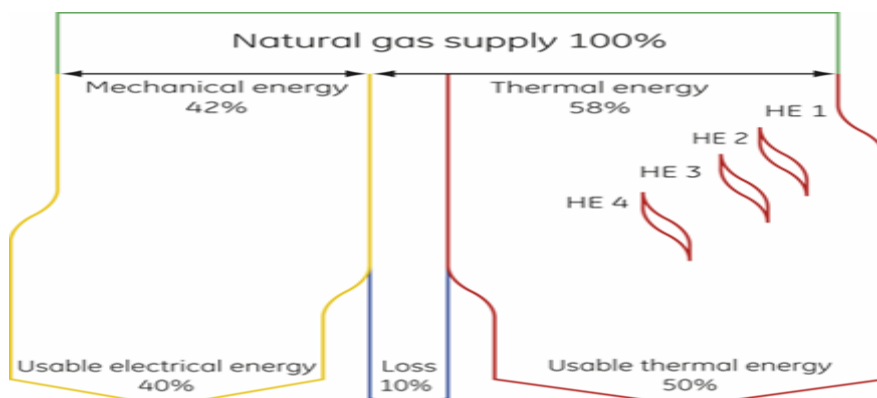
In this case, energy density for the plasma operation is supplied through gas engine with 38% of efficiency and remainder syngas of 9.34 MW can be burned directly. This sceneria is shown below on figure 18:



*Figure 18: Fuel gas application with Gas-Engine integrated*

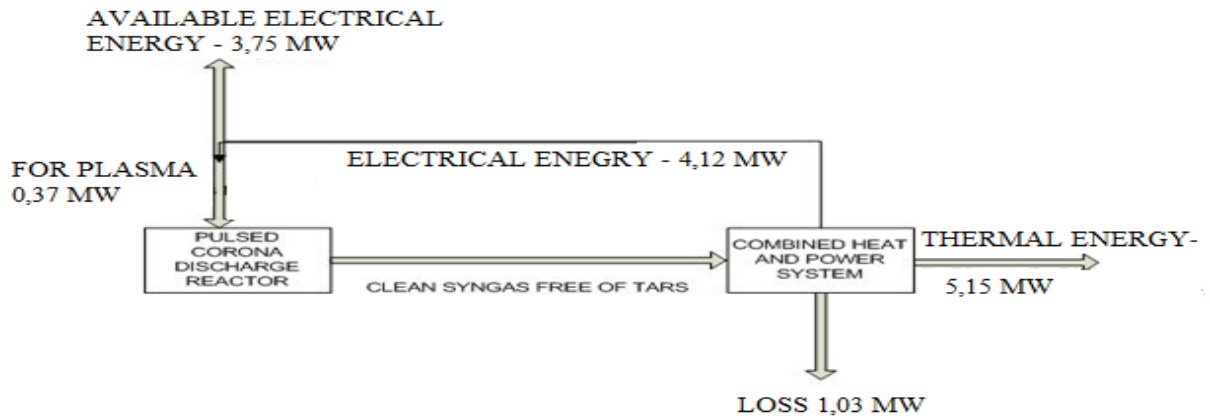
**4.3.2.2. Case 2: Combined Heat-Power (CHP)**

The combined heat and power (CHP) is the simultaneous production of electricity with the recovery and utilisation of heat. Having such arrangement would allow production of electricity for the plasma operation and rest syngas being used for heating through co-generation as it is a highly efficient form of energy conversion. For the CHP applications, a variety of different fuels can be used to facilitate co-generation. It can be either natural gas, bio-gas or fuel gas. The overview of such co-generation system is shown below on figure 19:



*Figure 19: CHP system efficiency of GE, He 1- Mixture, He 2- Oil exchange, He 3- Engine jacket water heat exchanger, He 4- Exhaust gas heat exchanger [85]*

It can be seen that 10% is accounted for the loss and rest being converted either to electricity or useable thermal energy as the heat source from the gas engine is utilized. Therefore, with CHP system integrated and utilization of the clean syngas from the plasma reactor would be used in following arrangements:



**Figure 20: Fuel gas application with combined heat and power system**

Consequently, it can be seen that having CHP system integrated in the fuel gas application would provide 5.15 MW of thermal energy and 4.12 MW of electrical energy. However, such arrangement gives reduced amount of thermal energy (5.15 MW) versus the gas engine installed case (9.34 MW). Therefore, depending on the priority as to whether thermal or electrical or even both are needed, integration of only gas engine or CHP system can be decided.

As a result, the syngas generated from small-scaled fixed-bed gasifier and tar reformed through non-pulsed corona discharge plasma unit is found to be only suitable as fuel gas to generate heat or electricity. From this point on, term fuel gas will be utilized throughout the report.

#### 4.4. SENSITIVITY ANALYSIS

In the previous parts, simulation of non-pulsed corona discharge plasma reactor with small-scaled fixed-bed gasifier gave syngas free of tars with composition suitable for fuel gas for heat or electricity generation. This is an indication that integration of plasma reactor with gasifier is technologically possible. However to simulate the plasma operation on aspen plus software, few assumptions had to be made due to lack of literature source, which are:

1. At the given energy density, the tar reforming were more than 95%. To account for the inefficiency (5%), it is assumed that the 5% of the carbon in the tar stays within the produced syngas as carbon. Such residue of carbon need to be separated before the tar free syngas gets sent to its application.
2. The oxygen radical from CO<sub>2</sub> dissociation can get terminated by the hydrogen presence in the syngas to make water. In ideal situation, no oxygen radical should react with hydrogen and to account for oxygen radical termination by hydrogen, it is assumed that 5% of the available oxygen radical gets terminated to produce water.
3. The supplied energy density is enough to reform the tars into lighter hydrocarbons, which means tar reforming does not produce syngas components like CO or H<sub>2</sub>. However, the term light hydrocarbons are assumed to be methane and all the tar components are reformed to make methane.
4. The available literature research claims that the 50% of the syngas entering the plasma reactor should be of nitrogen gas. The only source of nitrogen for above proposed cases are from the air, which is used as gasifying agent during the coal gasification. For the small-scaled gasifier,

the steam/oxygen (air) ratio at 0.8 gives only 44% of the total syngas entering the plasma reactor to be nitrogen gas. Therefore, it is assumed that 44% percentgae of nitrogen were enough to reform the tars , although the study papers claim more (>50%) nitrogen content in the gas allows higher tar reforming efficiency.

5. During plasma operation, the tar gets oxidized by the oxygen radicals formed from CO<sub>2</sub> dissociation through high energy nitrogen electrons. It is unclear as to how much of CO<sub>2</sub> the syngas to be cleaned has to contain. Thus, it is assumed that the CO<sub>2</sub> produced from the coal gasification from ambient fixed-bed gasifier is enough for plasma to reform the tars.

It has been seen from the considered applications that the clean syngas from the plasma reactor is only suitable for fuel gas to either generate electric or thermal energy due to mainly high content of nitrogen gas. For this application, the overall energy stream (MJ/hr) is important and some of the above mentioned uncertainties are taken into account for sensitvity analysis to see how slight change of these uncertainties affect the overall energy stream (MJ/hr) of the fuel gas.

**Free carbon (5%):** The 5% of the carbons in the tar were by-passed over the plasma reactor to account for the tar reforming inefficiency. The table below summarizes how conversion of the carbon in the tar affects the syngas exiting the plasma.

**Table 22: Effect of carbon by-pass percentage increase on fuel gas composition and on its energy stream**

Carbon bypass (%)	KMOL/HR												LHV(M J/m <sup>3</sup> )	Volume (m <sup>3</sup> /hr)	Energy stream ( MJ/hr)
	C	O	H	N <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> S	COS	NH <sub>3</sub>	HCN			
0	0	0	51.19	67.72	18.92	34.52	30.01	6.5	0.1	0.01	2	0.47	7.90	4728.68	37121.48
<b>5 (B.C)</b>	<b>0.68</b>	<b>0</b>	<b>52.55</b>	<b>67.72</b>	<b>18.24</b>	<b>34.52</b>	<b>30.01</b>	<b>6.5</b>	<b>0.1</b>	<b>0.01</b>	<b>2</b>	<b>0.47</b>	<b>7.78</b>	<b>4769.69</b>	<b>37108.19</b>
10	1.36	0	53.91	67.72	17.56	34.52	30.01	6.5	0.1	0.01	2	0.47	7.70	4789.65	36880.29
20	2.72	0	56.63	67.72	16.20	34.52	30.01	6.5	0.1	0.01	2	0.47	7.51	4850.61	36428.11
30	4.08	0	59.35	67.72	14.84	34.52	30.01	6.5	0.1	0.01	2	0.47	7.34	4911.58	36051.00
40	5.44	0	62.06	67.72	13.48	34.52	30.01	6.5	0.1	0.01	2	0.47	7.16	4972.32	35601.82
50	6.80	0	64.78	67.72	12.12	34.52	30.01	6.5	0.1	0.01	2	0.47	6.98	5033.29	35132.35
60	8.16	0	67.50	67.72	10.76	34.52	30.01	6.5	0.1	0.01	2	0.47	6.81	5094.25	34691.87
70	9.51	0	70.22	67.72	9.40	34.52	30.01	6.5	0.1	0.01	2	0.47	6.65	5155.00	34280.72
80	10.87	0	72.94	67.72	8.04	34.52	30.01	6.5	0.1	0.01	2	0.47	6.49	5215.96	33851.59
90	12.23	0	75.66	67.72	6.68	34.52	30.01	6.5	0.1	0.01	2	0.47	6.33	5276.93	33402.95
100 ▼	13.59	0	78.38	67.72	5.32	34.52	30.01	6.5	0.1	0.01	2	0.47	6.18	5337.89	32988.1 ▼

It can be seen that increasing the free carbon by-passed percentage to account for plasma reactor’s inefficiency results lower energy stream (MJ/hr) of the fuel gas due to decreased low heating value of the fuel gas. For the actual plasma simulation, the free carbon bypassed were at 5%, which is reffered as base case (BC) shown on the above table. In order to determine whether 5 percentage were good approximate, the carbon by-pass percentages at 0, 5 and 10 are considered and compared as follows:

Carbon bypassed (%)	Volume (m <sup>3</sup> /hr)	LHV (MJ/m <sup>3</sup> )	Energy stream (MJ/m <sup>3</sup> )	MW	Change in %
0	4728.68	7.90	37121.48	10.31	100
<b>5 (BC)</b>	<b>4769.69</b>	<b>7.78</b>	<b>37108.19</b>	<b>10.30</b>	<b>99.90</b>
10	4789.65	7.70	36880.29	10.24	99.32

Therefore, the complete tar reforming (0% carbon by-passed) results energy stream of 37121.48 MJ/hr, while the base case (5%) gives 37108.19 MJ/hr, which is 99,90% of the maximum possible energy

stream. Increasing the carbon percentage by-pass to 10% results 0.58% less energy stream than the base case and 0,68 % less than the maximum possible energy stream. Thus, it can be said that approximation at 5% is not sensitive and increase/decrease does not improve the energy stream (MJ/hr) significantly. In general, increase in carbon by-pass percentgae (higher inefficiency) results low energy stream (MJ/hr) and this is due to mainly reduced amount of methane in the syngas, hence lower low heating value. While, methane amount is decreased, the hydrogen in the syngas increased as it is not consumed by the carbon. However, change is methane amount in this case is main reason for decreased energy stream due to increased tar reforming inefficiency.

**Oxygen radical termination:** On the aspen simulation of plasma operation, terminations of the oxygen radicals from CO<sub>2</sub> dissociation by hydrogen from the syngas to form water were reflected. For that, 5% of the total oxygen radicals were terminated resulting water formation. Such effect reduces the hydrogen content in the syngas and increases the water content. In ideal situation, no oxygen radical should be terminated by hydrogen presence and worst situation would be to have all the oxygen radicals (100%) reacting to form water (no tar reforming). The table 23 below shows the syngas exiting the plasma where different percentages of oxygen radicals are terminated by hydrogen in the fuel gas.

**Table 23: Effect of increased oxygen radical termination by the hydrogen in the fuel gas**

Oxygen radical reaction (%)	0%	5%(B.C)	10%	100%	
				Fuel gas	Tar
CARBON (C)	0.68	0.68	0.68	0.00	13.59
OXYGEN (O)	0.00	0.00	0.00	0.00	0.66
HYDROGEN (H)	54.13	52.55	50.97	60.48	17.08
NITROGEN (N <sub>2</sub> )	67.72	67.72	67.72	67.72	007
METHANE (CH <sub>4</sub> )	18.24	18.24	18.24	6.65	-
CARBONMONOXIDE (CO)	32.94	34.52	36.10	31.62	-
CARBONDIOXIDE (CO <sub>2</sub> )	31.59	30.02	28.43	31.59	-
WATER (H <sub>2</sub> O)	4.91	6.5	8.07	4.92	-
SULPHUR (S)	0.00	0.00	0.00	0.00	0.03
HYDROGEN-SULFIDE (H <sub>2</sub> S)	0.10	0.10	0.10	0.07	-
CARBONYL-SULFIDE (COS)	0.01	0.01	0.01	0.01	-
AMMONIA (NH <sub>3</sub> )	2.00	2.00	2.00	1.86	-
HYDROGEN-CYANIDE (HCN)	0.47	0.47	0.47	0.47	-
Volume (m <sup>3</sup> /hr)	4769.75	4769.69	4769.75	4603.39	704.70
LHV (MJ/m <sup>3</sup> )	7.77	7.78	7.79	6.28	-
Energy stream (MJ/hr)	37060.98	37108.19	37156.35	28909.29	-

For this case, the oxygen radical termination percentages are chosen at 0, 5 and 10. The table 23 shows that more oxygen radical reaction results less hydrogen, CO<sub>2</sub> contents and more CO and water content. The oxygen radical termination does not affect the volume of the produced fuel gas and the methane content. This gives slight increase of low heating value of the fuel gas per cubic meter, hence slight higher energy stream (MJ/hr). Such approach is not appropriate as the oxygen radical termination by hydrogen only affects the H, CO, CO<sub>2</sub> and Water content in the fuel gas. However, in reality higher oxygen radical termination means lower methane formation due to less tar reforming and this will give reduced amount of overall energy stream. Due to lack of literature information for change in methane formed due to oxygen radical termination, formed methane cannot be varied and were kept constant. Therefore, it does not allow to conclude that more oxygen radical termination increases the low heating value of the fuel gas, hence energy stream of the fuel gas. Furthermore, data analyzing at 0 or 5 and 100% oxygen radical termination would give general view as to how such change affects the energy stream of the fuel gas. Because 0% oxygen radical termination would mean maximum possible

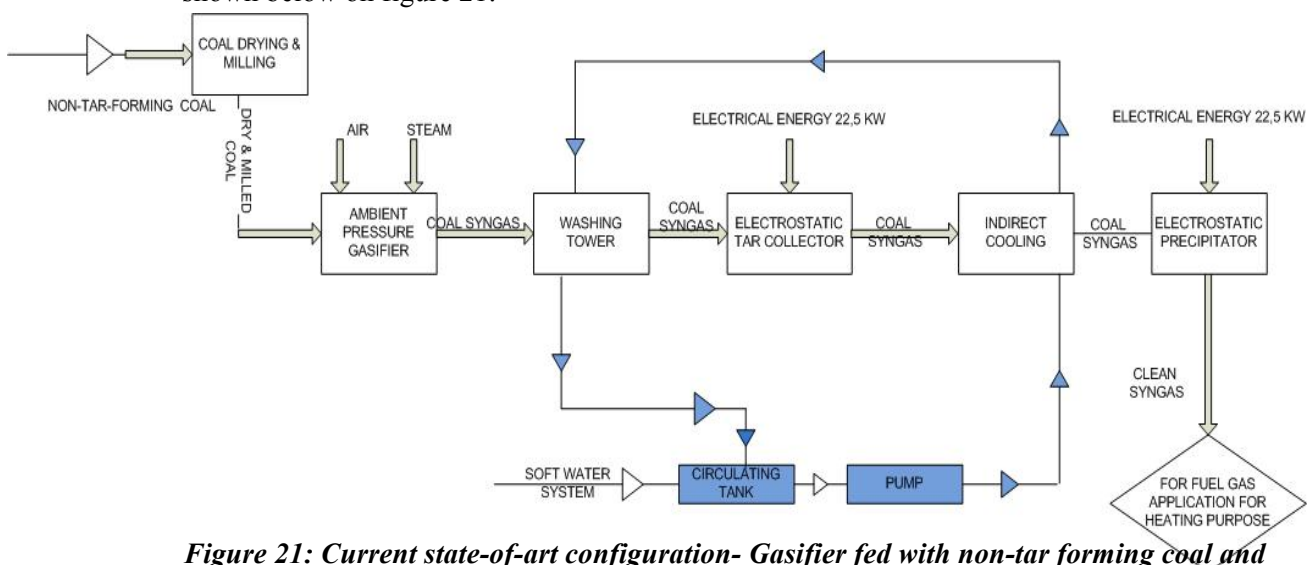
methane formation, no change in H<sub>2</sub>O, CO, CO<sub>2</sub> contents compared to that from the gasifier. 100% oxygen radical termination would mean no tar reforming at all and composition would be the same as one from the coal gasifier with tar content added in forms of carbon, oxygen and hydrogen. With these two points in mind, it can be seen that the overall energy stream (MJ/hr) is decreased at 100% radical termination. However, in plasma operation, such high percentage of oxygen radicals termination won't occur as it does have selectivity towards tar reforming rather than oxygen termination. If oxygen termination were to be taken into account, less than 10% is a good approximate and within 0 to 10% does not result significant change in overall energy stream.

**4.5. MARKET RESEARCH**

The tar containing syngas from atmospheric fixed-bed gasifier is technologically feasible to be treated by pulsed corona discharge plasma method and determined to be suitable as fuel gas for heat or electricity generation purpose. Before going any further, secondary market research needs to be performed in order to determine whether there are demands or need for such technology. Therefore the market research was conducted and the findings are presented in this section. The market research involves determining and assessing of the current state of art technology to tackle the tar problems, its competitiveness over proposing plasma involved method and determining of possible market size for the plasma method for tar cleaning.

**4.5.1. CURRENT-STATE-OF-ART**

The current-state-of-art utilizes atmospheric fixed-bed gasifier to generate fuel gas. However, to avoid the tar issues, the gasifier is often fed with non-tar forming quality coal, namely semi-Anthracite or Anthracite type coals. These coals are either expensive due to the high demand and are not widely available. Gasification of such type of coal still requires external cleaning units to meet their application purposes. The purpose of the cleaning units for this case is to remove very small amount of light tars (if present) and mainly dusts. This method makes use of fresh water for cooling, electrostatic precipitator and electrostatic tar collector to remove these impurities. Simplified block flow diagram of the current state of art configuration is shown below on figure 21:



**Figure 21: Current state-of-art configuration- Gasifier fed with non-tar forming coal and multi electrostatic/water based fuel gas cleaning for gas cleaning [84]**

The first problem of the current state of art case is the use of only high ranked or very small amount of light tar forming coals as they are not widely available and/or are very expensive. In addition, the electrostatic precipitator and tar collector units are integrated with cooling tower in the current state of art configuration. Water is used for cooling and is in direct contact with the fuel gas to be cleaned. This type of fuel gas cleaning method is not environmentally



friendly and requires the polluted water to be treated. On the other hand, multi-stage fuel gas cleaning units can be replaced by pulsed-corona-discharge plasma reactor, which allows feeding of the gasifier with low quality, tar forming coals as the plasma unit reforms the tar content in the fuel gas and these type of coal costs lower than the non-tar forming coals. The tars get reformed, which then improves the heating value of the fuel gas, which is favoring for heat generation fuel gas. When using plasma tar cleaning, the direct contact of water and the fuel gas is avoided. Therefore no wastewater is produced. The potential market for small-scaled fixed-bed gasifier and plasma reactor for the determined application will exist depending on the heat demand or energy policy of potential countries. For the market research, countries with high coal consumption, or countries with high development of coal industries are closely looked.

**4.5.2. FEASIBILITY OF FIXED-BED GASIFIER AND PULSED CORONA DISCHARGE PLASMA**

Market research for the studied technology (fixed-bed gasifier/plasma) is researched based on available literature on the internet for space or any other possible heating purpose in China and India.

**PEOPLE’S REPUBLIC OF CHINA (PRC):** Today, China still uses fuel gas in hundreds of cities. Chinese very first fuel gas factory and the delivery system were constructed in 1865 in the Shanghai international Settlement by British entrepreneurs. Introduction of further fuel gas factory and delivery system were build in Machhuria, Northeast between year of 1907 and 1934. The demand for fuel gas had expanded rapidly from 0.34 million cubic meters in 1949 to 1925 million cubic meters in 1978, which is a period of Chinese economy isolated from the western world, where the economic growth were at low rate in comparison to that for China. As a result of using the supplied fuel gas instead of traditional coal burning for cooking and heating brings various advantages, which include better indoor air quality, better public health and more convenient. Therefore, such shift from coal burning at home to use of fuel gas supply was encouraged by the State Council, China’s chief administrative authority in 1984. Such facilitation lead to 147 cities having fuel gas supply pipelines in 1994 and 51 cities has natural gas supply systems [87-89]. However, the continuous growth of fuel gas usage in China lasted until 2009 and started to decline as the country started to shift from fuel gas to natural gas as the fuel gas lost its competitive advantage over natural gas when coal price went up rapidly. Such decline is expected to continue for many cities across China. For instance, City Shanghai is expected to completely shift to natural gas by the end of 2015 and Beijing had completed its conversion completely back in 2006. The figure 22 below shows the trend of residential consumption of different gases:

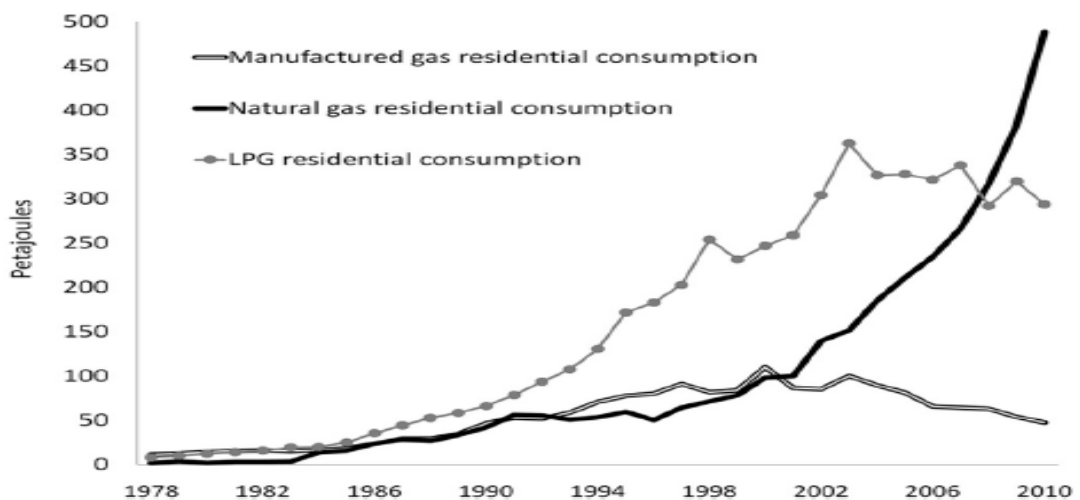
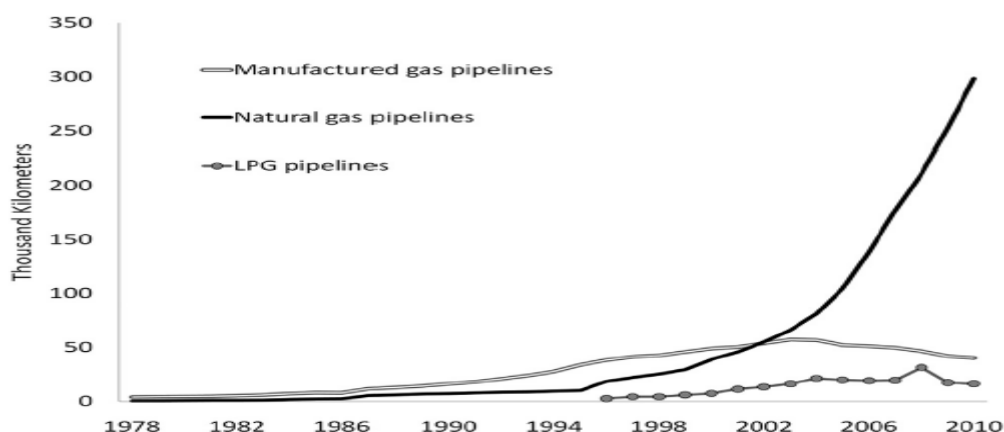


Figure 22: Residential gas consumption in China [87]



The figure 23 below demonstrates the fuel gas, natural gas and LPG pipelines status in China up until 2010.



**Figure 23: Fuel gas pipelines in China [87]**

It can be seen from the above figure 23 that the pipelines for fuel gas are declining, while one for the natural gas is increasing. This indicates that natural gas will be used for residential areas for heating purposes, leading the role of fuel gas in residential areas to decline. As of 2015, China is giving more importance to SNG (synthetic natural gas), which is coal-based natural gas. This can be seen by the fact that there are several large scaled coals to natural gas projects operating, planned. In December 2013, China’s first two natural gas factories started their commercial operations, which are Qinghua’s plant in Xinjiang and Datang Power’s Keqi plant in Inner Mongolia. There are in total 4 large natural gas production projects planned, which are to meet Beijing’s natural gas demand. The demand for natural gas by the end of 2015 is predicted to be between 15-18 million cubic meters [89, 93]. Apart from these coals to natural gas projects, there are 20 other natural gas projects that have obtained the approval from the National Development and Reform Commission (NDRC), which 13 of them are conditional approval. Having all these natural gas projects implemented successfully would lead 83.3 billion cubic meter of natural production. The summary of natural gas projects (operating, planned) are shown below on table 24:

**Table 24: Coal to Natural gas projects in China [89]**

Company	Location	Capacity (bcm/y)	Project status
Approved in 2009/10			
Datang International Power Generation	Keqi, Inner Mongolia	4	Operation
Qinghua group	Yili, Xinjiang	5.5	Operation
Datang International Power Generation	Fuxin, Liaoning	4	Construction
Huineng Coal Chemical Co	Ordos, Inner Mongolia	1.6	Construction
<b>Total 1 (bcm/y)</b>		<b>15.1</b>	
Approved in 2013/14			
Datong Coal Mine Group , CNOOC	Datong, Shanxi	4	Approved
SDIC Xinji Energy Co	Anhui, Huainan	2.2	Approved
China power investment	Huocheng, Xinjiang	6	Approved
Xinwen Mining group	Yili, Xinjiang	2	Approved
Sinopec, Huaneng Xinjiang Energy development Co	Changji, Xinjiang	8	Approved

Henan Energy and Chemical Industry	Changhi, Xinjiang	4	Approved
Suxin Energy	Changji, Xinjiang	4	Approved
Xinjian Guanghui	Changji, Xinjiang	4	Approved
China coal	Changji, Xinjiang	4	Approved
Huaneng Group	Changji, Xinjiang	4	Approved
China Huadian	Changji, Xinjiang	6	Approved
Xinmeng energy	Ordos, Inner Mongolia	4	Approved
Beijing Enterprises group	Ordos, Inner Mongolia	4	Approved
CNOOC	Ordos, Inner Mongolia	4	Approved
Hebei Construction and Investment	Ordos, Inner Mongolia	4	Approved
China Guodian1	Xinganmeng, Inner Mongolia	4	Approved
<b>Total 2</b>		<b>68.2</b>	
<b>TOTAL (bcn/y)</b>		<b>83.3</b>	

To get the final approval from the NDRC, construction of natural gas pipelines from the project site to the target market is crucial as most of these projects are remotely located from the target market. Therefore, development of natural gas transmission pipelines, as well as the required infrastructure will be the main role in successful development of natural gas industry in China. Moreover, it can be seen from above that 60% of the project is located in Xinjiang, which is far from the main consuming areas in China.

The brief touch on coal to natural gas development status in China helps to conclude that there is no potential market for fuel gas for residential area for house heating purposes. However, while natural gas pipeline is being constructed, the old pipelines used for fuel gas transportation is being dismantled and being brought to coal chemical industry sites to supply fuel gas for industrial purposes for heating as there are rapid growth in large scaled coal chemical projects close to the coal source across China. As a result, it reduces the capital cost for the project, as these projects are remotely located from the residential area. This is an indication that there is a fuel gas usage potential in industrial purposes and table 25 below gives overview of heating source and consumption by areas of China in 2013.

**Table 25: Heat production and consumption by area in China [91]**

Heating source	Heat amount (TJ)	%
Coal	3353067	91.2
Oil	112017	3.1
Gas	134618	3.7
Biofuels	11543	0.3
Waste	34912	1.0
<b>Total production</b>	<b>3646157</b>	<b>100</b>
<b>Consumption</b>		
Industry	2181842	69.0
Transport	0	0
Residential	814720	25.8
Commercial and public services	74490	2.4
Agriculture/forestry	11886	0.1
Fishing	0	0
Other non-specified	90759	2.9
<b>Total consumption</b>	<b>3162997</b>	<b>100</b>

Therefore, it can be seen that 91.2% of the total produced heat is sourced from coal in 2013, which 344 kt Coking coal and 226752 kt of sub-bituminous coal were consumed to generate 3353067 TJ of heat. On the other hand, 69% of the heats were used by the industries, which is the potential area for fuel gas usage for heating. Therefore, feasibility of fixed-bed gasifier and non-thermal plasma to generate clean fuel gas is present, hence to supply the heat needed for industries (2181842 TJ).

**LARGE GASIFIER CASE-26400 kg/hr (daf) COAL AS FEED**

The table 26 below shows the syngas specifications exiting the plasma with their hourly, yearly production amounts together with coal consumption amount.

*Table 26: Syngas specification exiting the plasma from small gasifier case*

<b>LHV (TJ/m<sup>3</sup>)</b>	<b>0.000944</b>
<b>Fuel gas (m<sup>3</sup>/hr)</b>	<b>68970.92</b>
<b>Coal (kg/hr)</b>	<b>26400</b>
<b>Fuel gas (m<sup>3</sup>/y)</b>	551767360
<b>Heat (TJ/y)</b>	<b>52086.84</b>
<b>Coal(t/y)</b>	<b>211200</b>

The produced fuel has low heating value of 0.0000944 TJ/m<sup>3</sup> and 1 unit of large scaled gasifier produces 551767360 m<sup>3</sup> of syngas yearly and such amount of syngas with mentioned heating value is able to generate 52086.84 TJ of heat yearly. To supply the industrial heat demand, in total of 41 gasifiers coupled with plasmas are needed to clean the fuel gas generated from chosen large scaled gasifier

**SMALL CASE-1500 kg/hr (daf) COAL AS FEED**

The clean fuel gas specification resulting from ambient fixed-bed gasifier/plasma is shown below on table 27:

*Table 27: Syngas specification exiting the plasma from small gasifier case*

LHV (TJ/m <sup>3</sup> )	0,0000078
Fuel gas (m <sup>3</sup> /hr)	4321.34*
Coal (kg/hr)	1500
Fuel gas (m <sup>3</sup> /y)	34570720
Heat (TJ/y)	268.96
Coal(t/y)	12000

\*Syngas needed to supply plasma energy is deducted

Due to its size, it requires 8112 small-scaled fixed-bed gasifiers and 8112 plasmas to generate fuel gas, hence to supply the heat demand in industries.

Furthermore, it can be seen from both cases that less amount of high pressure large scaled gasifiers (41 units) are needed to supply the industrial heat demand and this once again proves infeasibility of the large gasifier on top of what it was earlier concluded due to large electrical energy demand for air compressors to supply the gasifying agents at 30 bars. On the other hand, lot of small scaled ambient pressure gasifiers are needed (8112 units). This leads to conclude if plasmas are successfully developed and integrated with ambient fixed-bed gasifiers, there is market for it. In regards to accuracy of the estimate of this market research, the given numbers are trustable. According to the Air-Liquide’s internal marketing study, it was found in total 3000 ambient fixed-bed-small scaled gasifiers are needed for heating purposes. Above calculation gave 5112 gasifiers more and this can be explained by the fact

that such amount of gasifiers are needed for steam heating, while the remaining 3000 is used as space heating.

**INDIA:** The heat data used for China were obtained from International energy agency portal and the obtained data are the possible latest information and corresponds to year 2013. However, heat production/consumption data for India were not published on the same source. Therefore, Indian population and GDP in 2013 were used to relate it to Chinese heat production/consumption for industrial purpose, hence, the demands for fixed-bed-gasifier and plasma units were estimated.

**Table 28: Indian heat consumption estimation [91, 92]**

CHINA DATA (2013)	CHINA DATA (2013)	INDIA DATA (2013)
Population	1360000000	1250000000
GDP (\$)	9490600000000	1875160000000
Total heat consumption (TJ)	3162997.00	574400.15

Therefore, by correlating the population and GPD of India to that for China, the heat consumption is estimated to be 574400.15 TJ and such amount can be assumed as total demand for industrial purpose as no heat is needed for residential heating purpose. To generate such amount of heat, in total **2135** ambient fixed-bed gasifier and **2135 plasma units** are needed for fuel gas application.

**RUSSIA:** Another approach to define potential market for the gasifier and the plasma units, countries consuming/ producing largest amount of coal can be looked at. According to the International Energy agency’s 2015 statistics on Coal information, Russia ranked third largest coal consumer country within the non-OECD countries [2]. Although Russia is placed higher in coal consumption ranking, enormous proven reserves of natural gas in Russia automatically makes the fuel gas produced through coal gasification option infeasible and that there is no market for it. Moreover, according to International Energy Agency’s 2015 statistics on natural gas information, the major area of natural gas final consumption for non-OECD countries are in order of residential, commercial and public services, pipeline transport, oil refineries, chemical and Petrochemical and iron and Steel etc. [93]

In 2013, Russian federation produced 5413017 TJ of heat from various sources, which 20% is from coal and 65% from gas. In the same year, the country consumed 4520206 TJ of heat for various final consumptions, which 36% were for industrial purpose and 47% were for residential areas. Therefore, competitiveness of fuel gas for heat generation is not present, given that there are enough natural gas reserves [92].

**4.6. ECONOMIC COMPETITIVES OF PLASMA TECHNOLOGY IN FUEL GAS APPLICATION**

The market research in the previous part has indicated that there are markets for the studied integrated technology for fuel gas generation in China and India. Therefore, the research continued to determine whether there is an economic competitiveness for the purposing plasma involved fuel gas generation technology over the current state of art technology to generate fuel gas in China. To start the economic analysis for the plasma based fuel gas generation, companies providing complete fuel gas generation system by means of ambient fixed-bed gasifier, syngas cleaning units (tar, dust, sulfur) in China were found on the Alibaba (<http://www.alibaba.com/>), China’s biggest online commerce company. Request to provide quotation for the defined scope was sent and the scope included feeding the gasifier with enough coal to give syngas. Detailed quotations outlining variety of information, starting from coal specification to feed the gasifier until clean fuels gas to supply to the gas engine and their costs were received. The table 29 below summarizes the information relating to the economics, which are useful to make the economics for the plasma-based configuration:

**Table 29: Proposals summary obtained through Alibaba site- Original proposals can be found in the appendices [85]**

Supplier	Gasifier model/type	Gasifier	Gas cleaning	Desulfurization	Total CAPEX(\$)	BASE/ Process	Syngas composition	Note
Wuxi Teneng Power Machinery CO., LDT.	2.6 M dry gasification system, Double stage fixed bed gasifier	380.000			380.000	<b>Ex-Factory</b> Non-caking or weak-caking bituminous coal, Wind and Dry cooling for gas purification ( electrostatic precipitator included in the proposal) and other details are unknown	<b>CO:</b> 24-30 % <b>CO<sub>2</sub>:</b> 4-6 % <b>N<sub>2</sub>:</b> 47-51% <b>H<sub>2</sub>:</b> 13-15% <b>CH<sub>4</sub>:</b> 1,8-2,4% <b>O<sub>2</sub>:</b> < 0,6%, LHV: 5.2-5.4, 3800-4800 Nm <sup>3</sup> /h	The provided CAPEX were not separated into gasifier and desulfurization, although the price covers both.
Tangshan Keyuan Environmental Protection Technology and Equipment Co., Ltd	KM5Q3,2 Clean gas stations	98.200	183.800	159.000	440.400	<b>FOB Tianjin</b> 1: Gasifier, 2: Washing Tower, 3: Electric tar collector, 4: Indirect cooler, 5: Electrostatic precipitator, 6: Gas compressor	7000-8000 Nm <sup>3</sup> /hr, LHV 1450 kcal/Nm <sup>3</sup>	
Zhengzhou Sinoder Indutech Machinery Co., ltd	CG1Q3,2-21B, 3.2 m Coal gasifier system	160.000		Is not included in the proposal	160.000	<b>FOB Tianjin</b> Syngas from upper stages goes to Electrical tar precipitator and syngas from lower stage goes to Cyclone dust catcher	Gas LHV 5,2-5,4 MW, 6300-7800 m <sup>3</sup> /hr,	CAPEX for desulfurization and gas cleaning were not included in the proposal
Henan Hongji Mine Machinery CO., LTD	3,0 Double-stage Coal Gasifier+TOP/ Bottom gas cleaning	78.500	111.500	Is not included in the proposal	190.000	<b>EXW Zhengzhou</b> Gasifier is connected to TOP (Electric tar, Water seal Tank) and Bottom syngas cleaning (Gravity Dust, cyclone dust collectors, air cooler and water cooling tower). Followed by Final syngas cleaning (Electric tar arrester, water seal tank)	6000-7000 Nm <sup>3</sup> /hr	CAPEX for desulfurization and gas cleaning were not included in the proposal

It can be seen from the summary that the received proposals do vary in regards to overall proposal price, as their scopes are different. For example, one proposal includes the desulfurization unit, while the others don't. At times, it is unclear whether the proposal included the gas-cleaning units.

The most complete proposal were the from Tangshan Keyuan Environmental Protection and Equipment Co., Ltd as it covers what technology and units are included within the provided price offer and for what purposes they are present in the proposal. The proposal included cost breakdown for the each units and followings are the divisional prices:

**Table 30: Cost break-down of proposal- Tangshan Keyuan Environmental Protection Technology and Equipment Co., Ltd**

	Gasifier (\$)	Gas cleaning (Electrostatic tar cleaning / Tar precipitator) (\$)	Desulfurization (\$)
1	98.200	183.800	159.000
<b>Total (\$)</b>	<b>440.400</b>		

The table 30 above shows 22, 42 and 36 percentages of the total proposal cost are for gasifier, gas cleaning and desulfurization units respectively. The total proposal price is equal to \$440.400 and is at FOB base. These values will be used as the reference to compare the fuels gas production cost per m<sup>3</sup> for Alibaba current state-of-art case versus the current sold price of natural gas and LPG per m<sup>3</sup>. Because the natural gas and the LPGs are alternative to fuel gas for heat generation in China. The results will be used further as a reference to compare the production cost of fuel gas per m<sup>3</sup> from plasma-involved configurations based on the economic analysis.

Furthermore, for the plasma-involved configuration, gas-engine is needed to produce the electricity demand to support its tar reforming operation. This is specially the case for remote locations, such as mines, where supply of electricity is limited and needs self-electricity supplying solution. Therefore, integration of gas-engine is attractive when power from electricity grid is not available and to integrate the gas-engine price in the economic analysis, quotation for gas-engines through Alibaba site was obtained and the results are summarized below:

**Table 31: Gas-engine quotation summary for plasma configuration obtained through Alibaba site-Original quotations can be found in the appendices**

	Supplier	Gas engine model	CAPEX (\$)	BASE	Note
1	Shandong Lvhuan Power Equipment Co., Ltd	G12V190ZLT, prime power 500 kw	139.700	FOB Qingdao	Biomass gas engine
2	Shandong Dragon New Energy Co., Ltd	G12V190ZLDH-2, prime power 450 kW	130.521	FOB Qingdao	Coal gas based, remote fan cooler included
3	Mircale Power Systems Inc	MWM TBG620 L 450 MW	135.000	FOB Shanghai	Coal gas
4		Perkins 425 KW	207.000	FOB Shanghai	Biogas
5		MiracleGen/MPS 480 KW	63.120	FOB Shanghai	Biogas
6	Shangdong Chaiwei Power Equipment Co.,Ltd	CW-500GFH	132.256	FOB Qingdao	Coke Oven Gas

Based on above quotation prices, the gas engine price in plasma configuration will be considered as \$135 000 in China. Consequently, with the obtained capital costs for each units in fuel gas production for heat generation, preliminary economical analysis can be made for following three cases in order to assess their competitiveness against each other:



1. State-Of-Art case

- a. Atmospheric fixed-bed-gasifier
- b. Washing tower/Indirect cooling
- c. Electrostatic tar collector/ precipitator
- d. Purchase electricity

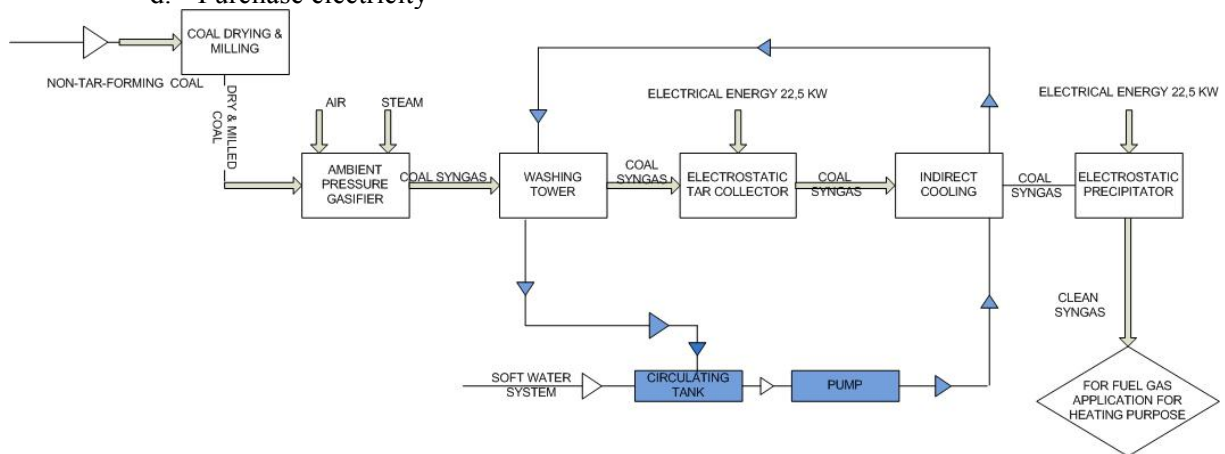


Figure 24: Current-State-of-Art configuration utilized in China to generate fuel gas for heating [85]

2. Plasma case without gas engine

- a. Atmospheric fixed-bed-gasifier
- b. Pulsed corona discharge plasma
- c. Purchase electricity

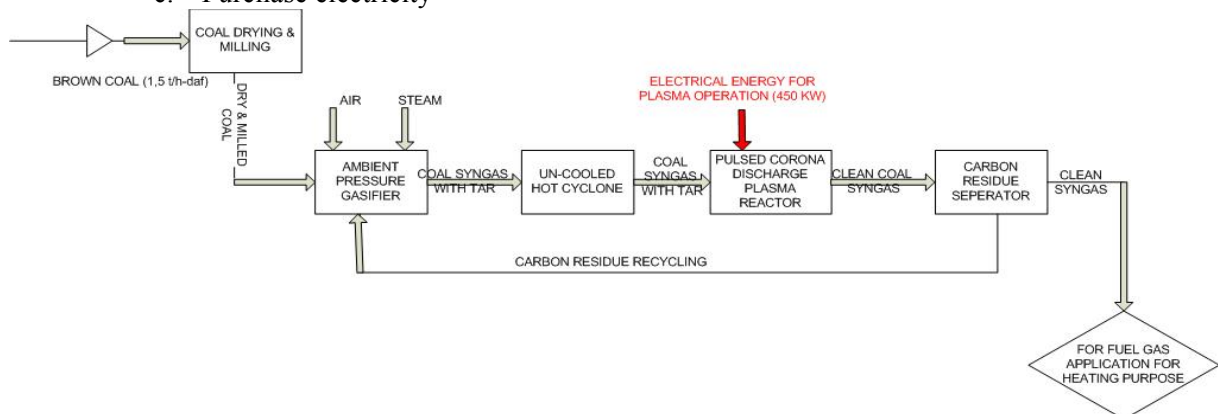


Figure 25: Proposing plasma configuration with no gas-engine integrated to supply plasma electrical energy

3. Plasma case with gas engine

- a. Atmospheric fixed-bed-gasifier
- b. Pulsed corona discharge plasma
- c. Gas engine to generate electricity (GI)

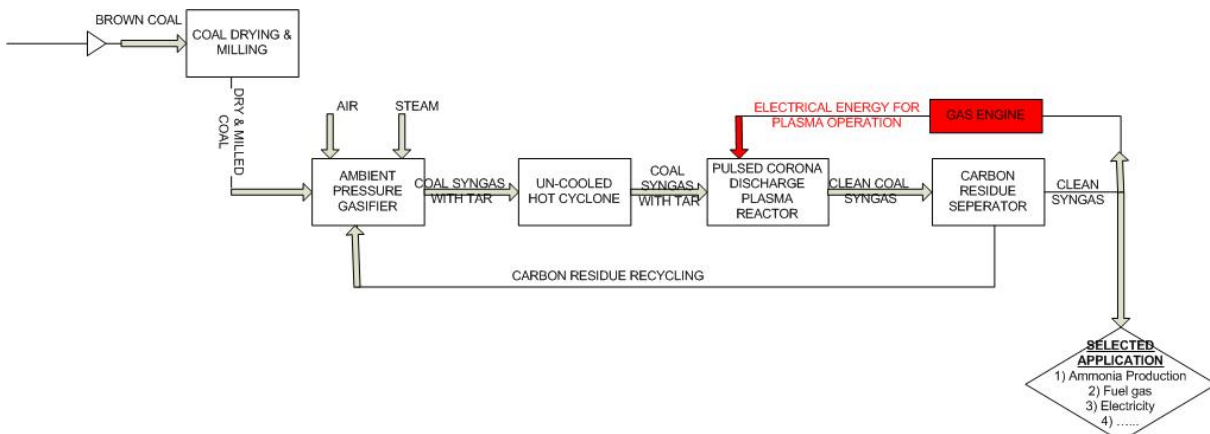


Figure 26: Proposing plasma configuration with gas-engine integrated to supply plasma electrical energy

**Table 32: Output comparison (MW) of State-of-Art (Alibaba), Plasma configuration with and without Gas-Engine against the current sold price of Natural Gas and LPG in China.**

Specifications	1:State-of-Art	2:Plasma w/o GI	3: Plasma w/ GI
Coal consumption (t/hr)-daf	1.50	1.50	1.50
Power consumption (KW)	37.00/94/	370.00	0.00
Annual operating hours (hr)	8000	8000	8000
<b>Utility costs</b>			
Coal cost (\$/t) <sup>2</sup> [90]	46.45	46.45	46.45
Electrical power cost (\$/kw) <sup>3</sup> [95]	0.05	0.05	0.05
Natural gas (\$/m <sup>3</sup> ) <sup>4</sup> -current sold price [95]	0.30	0.30	0.30
LHV Natural Gas/LHV Fuel gas (m <sup>3</sup> )	5.71	4.61	4.61
LPG price (\$/m <sup>3</sup> ) <sup>4</sup> -current sold price [95]	1.56	1.56	1.56
LHV LPG/ LHV Fuel gas (m <sup>3</sup> )	19.69	15.90	15.90
<b>Operating parameters</b>			
Syngas produced (Nm <sup>3</sup> /hr)	6007.47	4769.69	4321.34
Syngas LHV (MJ/m <sup>3</sup> )	6.28	7.78	7.78
Syngas LHV (MW)	0.0017	0.0022	0.0022
<b>Investment (\$)</b>			
Fixed-Bed-Gasifier (\$)	98200	98200	98200
Syngas cleaning (\$)	183200	0.00	0.00
Desulfurization unit (\$)	159000	159000	159000
Pulsed-corona plasma reactor (\$)	0.00	135000	135000
Gas engine (\$)	0.00	0.00	135000
TOTAL CAPEX (\$)	440400	392200	527200
<b>TOTAL INVESTMENT (\$) - CAPEX*4 [96]</b>	<b>1761600</b>	<b>1568800</b>	<b>2108800</b>
<b>Fuel gas production cost</b>			
Fixed cost (\$/hr)-25% of investment [96]	55.05	49.03	65.90
Coal (\$/hr)	69.68	69.68	69.68
Power (\$/hr)	1.99	19.95	0.00
Total (\$/hr)	126.72	138.65	135.58
Fuel gas cost (\$/m <sup>3</sup> )	0.021	0.029	0.032
Fuel gas cost/Natural gas cost (%)	<b>40.07</b>	<b>44.57</b>	<b>48.10</b>
Fuel gas cost/LPG cost (%)	<b>26.59</b>	<b>29.58</b>	<b>31.92</b>

It can be seen from the above table that, the total CAPEX at FOB base obtained from the received proposals is multiplied by cost indices of 4 to get the total installed costs (TIC) for above considered three cases. There is different specific international plant cost indices for each specific country and in specified years. For quick estimation, cost indices of 3.5-4 are the general value and are not specific to particular country or a year. Quick estimation with cost indices of 4 gives estimation accuracy of  $\pm 40-50\%$  [96].

The total CAPEX of the plant does not come for free and it should influence the fuel gas production cost per cubic meter. Therefore, the 25% of the TIC is taken in order to calculate the fuel gas production cost per cubic meter. Based on following assumptions, the 25% of the TIC is justified:

- It is assumed that the typical operating expectation is set at 12% of the TIC. Therefore, it gives 12% of yearly operating income, which is equivalent to 12% of the TIC. Such financial figure

is used by Air-Liquide to judge feasibility of the gas business. The yearly operating income should reach 12% in order for the business to be feasible.

- The remainder of the 25% accounts for the plant depreciation, which the plant (equipments) loses its value throughout the plant life-time and are depreciated over 15 years (6, 67%/year). It also includes the annual maintenance cost (3-4%) and the general operating administration costs.

As a result, it gives the analyzed capital cost, which indicates how much it would be annually, which for above case is 25% [96].

The current sold price (Dec, 2015) for natural gas, LPG, Coal and Electricity for industrial usage were obtained from Ebeijing (<http://www.ebeijing.gov.cn>), which is authorized by the Beijing Municipal Government and organized jointly by the Foreign Affairs office of the People’s Government of Beijing Municipality and the Beijing Network information industry office. With these prices obtained for China case, production cost per cubic meter of fuel gas from the State-of-Art (Alibaba) and Plasma configurations were found and compared against natural gas, LPG prices by considering the heating content of the fuel gases and determining the equivalent cubic meter of produced fuel gases from each cases that would balance the heat content of commercially sold natural gas and LPG. The table 33 below demonstrates the cost comparisons of above cases against the current market price for Natural gas and LPG:

**Table 33: Production cost comparison (\$/m<sup>3</sup>) of different cases against market price of NG and LPG**

	Market price (\$/m <sup>3</sup> )	Current state of art (\$/m <sup>3</sup> )	Plasma w/o GI (\$/m <sup>3</sup> )	Plasma w/ GI (\$/m <sup>3</sup> )
Natural gas	0.30	0.12	0.13	0.14
LPG	1.56	0.41	0.46	0.50

It can be seen that the fuel gas generated from the current state of art case costs less (0, 12 cent/m<sup>3</sup><sub>natural gas</sub>, 0, 41 cent/ m<sup>3</sup><sub>LPG</sub>) compared to current market price for the natural gas and the LPG. It can also be seen that the plasma-involved cases give also lower price compared to commercial natural gas and LPG. However, comparing the plasma configuration against the current state of art case, the fuel gas production cost is higher for both cases (with or without the gas engine integrated). Not integrating gas engine and purchasing electricity demand improves plasma case’s competitiveness against the current state of art case. As a result of above comparisons for the stated 3 cases, it is observed that in any case, heat generation through coal fuel gas is cheaper than burning natural gas or LPG in China. Moreover, competitiveness of fuel gas from plasm- involved case over current state of art case is negative.

Based on following assumptions, changes in the economic analysis are done in order improve the plasma configuration’s competitiveness against the the current State-of-Art case:

- The current state-of-Art case utilizes electrostatic tar collector and electrostatic precipitator methods to remove mostly the dust and at times light tars in the fuel gas. This is an indication that uses of feedstock are limited, as the coal at the lowest price would result heavy tars. Therefore, coal at the lowest price won’t be appropriate, while it can be used in the plasma case. Because the plasma method allows coal of lowest quality costing lot lower to be utilized and reforms the tar through plasma method. Therefore, cost comparison for plasma case against the current state-of-Art case should be compared at varied coal prices, which 46.45 \$/t-HIGH will be considered as the expensive coal (suitable for current state of art case) and 23.23 \$/t-LOW will considered as the cheap coal suitable for plasma case [90].
- Before deciding whether integration of gas-engine in plasma case is economical or not, analysis based on different electricity prices should be made. According to the used electricity price source, there are two different prices available for industrial purpose, which the lowest

is 0.054 \$/KW (0.35 Y/KW)-LOW, while the highest is 0.10 \$/KW (0.670 Y/KW)-HIGH. [95].

Consequently, the above two assumptions are integrated into the economical analysis and the outcome is compared against the State-Of-Art case. Because, having lower percentage for gas production per cubic meter than the State-Of-Art case is more crucial. The results of such changes in economic analysis are shown below:

**Table 34: Economic analysis for plasma case with various prices for Electricity and Coal**

<b>C O A L</b>	<b>W O L</b>	<ul style="list-style-type: none"> <li>• <b>NG: 39% (0.12 \$/m<sup>3</sup>)</b></li> <li>• <b>LPG: 26% (0.41 \$/m<sup>3</sup>)</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>NG: 33% (0.10 \$/m<sup>3</sup>)</b></li> <li>• <b>LPG: 22% (0.34 \$/m<sup>3</sup>)</b></li> </ul>
	<b>H I G H</b>	<ul style="list-style-type: none"> <li>• <b>NG: 50% (0.15 \$/m<sup>3</sup>)</b></li> <li>• <b>LPG: 34% (0.53 \$/m<sup>3</sup>)</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>NG: 45% (0.14 \$/m<sup>3</sup>)</b></li> <li>• <b>LPG: 30% (0.47 \$/m<sup>3</sup>)</b></li> </ul>
		<b>HIGH</b>	<b>LOW</b>
<b>ELECTRICITY (\$/KW)</b>			

The reference value for natural Gas is 40.07 % (0.12 \$/m<sup>3</sup>) and 26.59% (0.41 \$/m<sup>3</sup>) for LPG from the State-of-Art case. For the plasma case to be competitive against the current state-of-art case, the indicator percentage for natural gas and LPG should be as low as possible from 40.07 % and 26.59 % respectively. This is an indication that, the production cost of fuel gas from the plasma case is lower than that from current state-of-art case. As shown above, the HEHC (High-Electricity, High-Coal), LEHC (Low-Electricity, High-Coal) cases gave fuel production cost higher than that from the current state-of-art case, thus can be taken out of further consideration. On the other hand, HELC and LELC cases gave lowest production cost. Therefore, these two cases are considered further to improve the plasma case's competitiveness.

Now, the integration of gas-engine can be accessed on the HELC and LELC cases. However, it should be noted that having gas engine integrated in the configuration would mean no need of purchasing electricity from the central grid, which leaves to make analysis only for the LC (low-coal) case and results are:

**Table 35: Economic analysis for plasma case with various prices for coal and gas engine (Yes/No)**

<b>C O A L</b>	<b>W O L</b>	<ul style="list-style-type: none"> <li>• <b>NG: 36% (0.11 \$/m<sup>3</sup>)</b></li> <li>• <b>LPG: 24% (0.37 \$/m<sup>3</sup>)</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>NG: 33% (0.10 \$/m<sup>3</sup>)</b></li> <li>• <b>LPG: 22% (0.34 \$/m<sup>3</sup>)</b></li> </ul> Purchase of electricity at low cost
	<b>H I G H</b>	<ul style="list-style-type: none"> <li>• <b>NG: 48% (0.14)</b></li> <li>• <b>LPG: 32% (0.50 \$/m<sup>3</sup>)</b></li> </ul>	<ul style="list-style-type: none"> <li>• <b>NG: 51% (0.15 \$/m<sup>3</sup>)</b></li> <li>• <b>LPG: 34% (0.53 \$/m<sup>3</sup>)</b></li> </ul> Purchase of electricity at high cost
		<b>YES</b>	<b>NO</b>
<b>GAS ENGINE</b>			

It can be seen from the table 35 above that the case that gives the lowest gas production cost is when there is no gas engine integrated, meaning purchasing of the electricity need from the central grid at low cost and purchasing the gasifier feed also at 50% less than the coal fed to the current state of art

case. This results 33% (0.10 \$/m<sup>3</sup>) for natural gas, 22% (0.34 \$/m<sup>3</sup>) for LPG against 40.07% (0.12 \$/m<sup>3</sup>) for natural gas and 26.59 % (0.41 \$/m<sup>3</sup>) for LPG in the current state-of art case.

In addition, the capital cost for plasma unit was kept at the same price that for the gas engine (\$135 000) as a start. This is because plasma is a new technology and no reference price can be obtained. Use of prototype price in the economic analysis would not be realistic and can be too high. Therefore, it is the best to keep the plasma CAPEX as a variable and perform a sensitivity analysis. Now that all the possible factors/assumptions to reduce the fuel gas production costs from plasma case are considered, sensitivity analysis for the plasma unit is done by changing the plasma unit price starting from \$ 135 000.

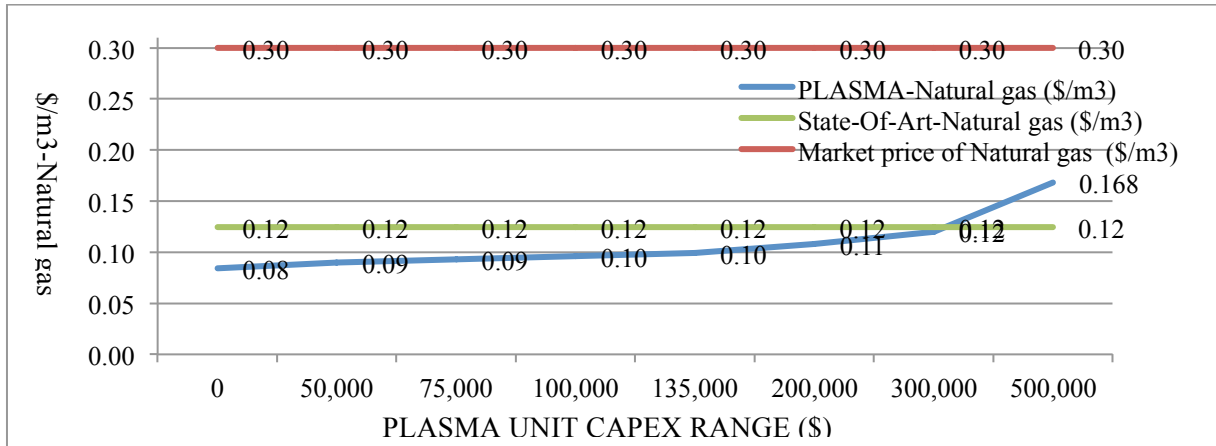


Figure 27: LELC case comparison against the State-of-Art case with varying plasma cost-Natural gas

It can be seen from figure 27 above that competitiveness of plasma case over current state of art case to generate fuel gas for heating increases as the capital cost for plasma unit decreases. Plasma case loses its competitiveness when capital cost for the plasma unit exceeds \$ 300 000.

Figure 28 below shows the same production cost comparison for the current state-of-art case and Plasma case for LPG against the current sold market price in China. It should be noted that, lowering the investment in the plasma unit provides lower fuel gas production against the state-of-art and the Market price of LPG cases.

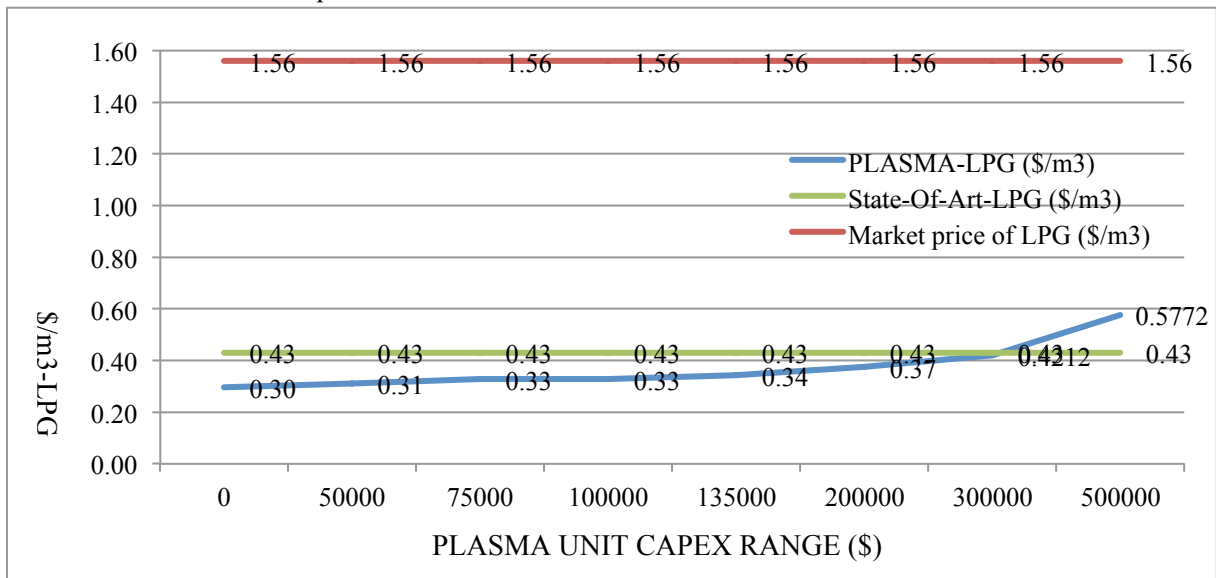


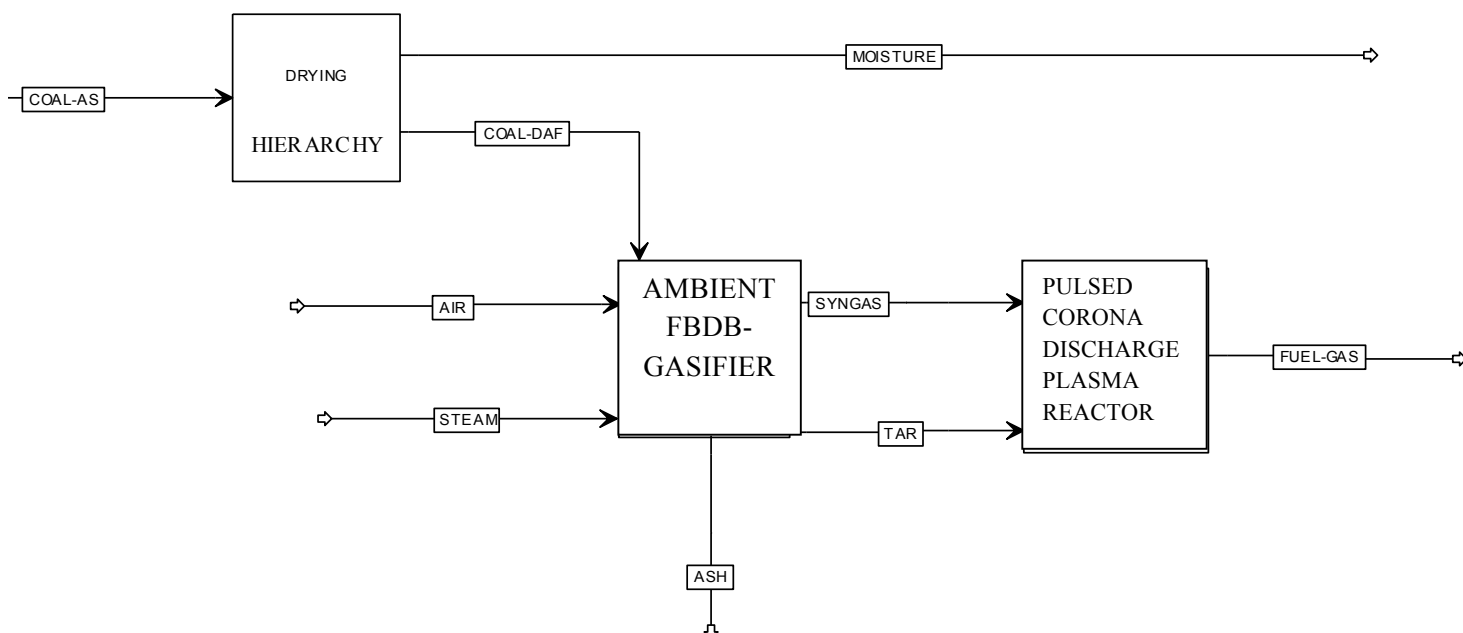
Figure 28: LELC case comparison against the State-of-Art case with varying plasma cost-LPG

Therefore, through the economic analysis, it has shown that replacing of the natural gas or LPG with fuel gas from coal gasification is economical for heat generation. Furthermore, this cost can be even further lowered by making changes in the current state-of-art case by replacing the multi-stages of fuel gas purification units with one single plasma unit. However, to ensure that the plasma unit offers such reduction in costs, following economical conditions should be met:

- 0.37 MW of electricity demand for the plasma tar reforming unit shall be supplied from the central electricity grid and purchased at 0.054 \$/KW (0.3495 Y/KW), hence no need for gas engine.
- The feed coal for the atmospheric fixed-bed-gasifier should be bought at 50% less than the price of the coal fed to the current state of art case. The gasifier coupled with the plasma unit does not limit the gasifier to be fed with low quality sub-bituminous coal, which is can be obtained at low price 50% reduced price than the price of anthracite coal.
- To improve the competitiveness of plasma case over the state-of-art case, capital investment in the plasma unit shall be carefully selected, which going down from \$300 000 improves the competitiveness. Therefore, more lower it is for the plasma unit from \$300 000, better competitiveness for the plasma configuration.



**4.7. PROCESS FLOW DIAGRAM FOR AMBIENT FIXED-BED GASIFIER COUPLED WITH NON-THERMAL PULSED CORONA DISCHARGE PLASMA REACTOR FOR FUEL GAS APPLICATION**



*Figure 29: Overall block-flow diagram of ambient FBDB small scaled gasifier integrated with non-thermal pulsed corona plasma discharge reactor for fuel gas generation for heating application*

**Table 36: Material balance for above shown overall simplified block flow diagram**

Mole Flow kmol/hr	COAL-DAF	SYNGAS	TAR	FUEL-GAS
CARBON (C)	86.10	0.00	13.59	0.68
OXYGEN (O)	21.00	0.00	0.66	0.00
HYDROGEN (H)	75.81	60.48	17.08	52.55
NITROGEN (N <sub>2</sub> )	1.24	67.72	0.07	67.72
METHANE (CH <sub>4</sub> )	0.00	6.65	0.00	18.24
CARBONMONOXIDE (CO)	0.00	31.62	0.00	34.52
CARBONDIOXIDE (CO <sub>2</sub> )	0.00	31.59	0.00	30.01
WATER (H <sub>2</sub> O)	0.00	4.92	0.00	6.50
SULPHUR (S)	0.12	0.00	0.03	0.00
HYDROGEN-SULFIDE (H <sub>2</sub> S)	0.00	0.07	0.00	0.10
CARBONYL-SULFIDE (COS)	0.00	0.01	0.00	0.01
AMMONIA (NH <sub>3</sub> )	0.00	1.86	0.00	2.00
HYDROGEN-CYANIDE (HCN)	0.00	0.47	0.00	0.47
<b>Total molar flow (kmol/hr)</b>	184.26	205.38	31.44	212.80
<b>Flow (m<sup>3</sup>/hr)</b>	4130.00	4603.39	704.70	4769.69
<b>LHV (MJ/m<sup>3</sup>)</b>	-	6.28	-	7.78
<b>Energy stream (MJ/hr)</b>	-	<b>28909.29</b>	-	<b>37108.19</b>
<b>Mass flow (kg/hr)</b>	1897.25	4537.29	221.99	4759.28

**4.8. PATENT SEARCH FOR COAL FUEL GAS CLEANING BY MEANS OF NON-THERMAL PULSED CORONA DISCHARGE PLASMA UNIT**

In the previous parts, it was determined that use of pulsed corona discharge plasma unit integrated with ambient fixed-bed gasifier is indeed technologically, economically feasible to generate fuel gas for heating purpose. In addition, the markets for such technologies were found to be present. Therefore, the study proceeded further to investigate whether there is any company or individual possessing patent right to use non-thermal pulsed corona discharge plasma for fuel gas generation through coal gasification.

As of today, there are patents for plasma based biomass tar removal embedded in the gasifier and coal gasification processes. However, there is no patent for coal fuel gas tar removal by non-thermal pulsed corona discharge plasma. The patent search using Patbase express ([https://www.patbase.com/express/search\\_basic.asp](https://www.patbase.com/express/search_basic.asp)) and Google patent ([www.google.com/patents](http://www.google.com/patents)) were conducted and relating findings are summarized below on table 37:

**Table 37: Patent search result for non-thermal pulsed corona discharge plasma method for fuel gas generation**

Patent #	Year	Applicant	Title	Note: Differences compared to pulsed corona discharge fuel gas cleaning application
US 9045337 B2	2015	Lai O.Kuku	<i>Waste material, coal, used tires and biomass conversion to alternative energy and synthetic fuels solutions system with carbon capture and liquefaction</i>	-The plasma torch is embedded in the feed gasifier -Oxygen as plasma gas
US 9150806 B1	2015	PHG Engery, LLC	<i>Microwave induced plasma cleaning device and method for producer gas-incorporated in the gasifier</i>	- Microwave induced plasma -Plasma takes role in the feed gasifier - No nitrogen gas is used in the plasma
JP 2003147 373	2003	Michio I., Noboru O	<i>Gasification of organic matter by using steam plasma</i>	-Steam plasma - Plasma incorporated in the feed gasifier
JP62797 69A2	1994	Hiromitsu M., Takeshi O.,	<i>Refining of coke oven gas by using pulsed corona-induced plasma chemical process</i>	-Applied for coke oven gas - Nitrogen gas is not used in the plasma creation
DE 3632105	1987	Sven S., Lindgren C.H.,	<i>Purification of coke over gas</i>	-Applied in coke oven gas cleaning - Thermal plasma created by heating up to 1560°C - Nitrogen gas us plasma heating gas to raise the temperature
JP 6184546 A2	1994	Mitsuhiro S., Katsuhiko S., Sakurai Y.,	<i>Reforming of tar by plasma irradiation for light components</i>	-Converting the high-boiling components of tar into low-boiling components -Subjecting to low temperature and high pressure -Low temperature plasma in a hydrogen containing atmosphere

DD2691 57A	1989	Hoffman H., Kleffe R., Koehler D.,	<i>Plasma reactor for pyrolysis of highly viscous, tarry, hydrocarbon containing products-Biomass</i>	-Cracking of hydrocarbon oils by electric means, electromagnetic or mechanical vibrations, by particle radiation or with gases superheated in electric arcs
NL 1024408	2004	Yan K.,	<i>Apparatus for generating corona discharges</i>	NA
KR 1011597 57	2012	Chamin Suk; Hur Min, Keel Sang In.	<i>Plasma reactor and tar or by- product and removing apparatus using the same-arc-plasma containing oxygen and steam</i>	-Arc plasma - Oxygen and steam are used in plasma creation

It can be seen that the patent to use non-thermal pulsed corona discharge plasma method for fuel gas tar removal is not possessed by anyone. Thus an invention disclosure for such application was filed.

**5. COAL GASIFICATION ASH HANDLING**

**5.1. REVIEW ON COAL COMBUSTION/GASIFICATION ASHES AND THEIR COMMERCIAL APPLICATIONS**

In the previous parts, it was shown that the gasification of brown coal through a small-scaled fixed bed gasifier is technologically feasible and it was determined that the production of fuel gas through the proposed case is competitive over the current state of art case for the purpose of heat and electricity generations. This was made possible through the help of pulsed corona discharge plasma for reforming the tar content in the fuel gas, which is more environmental process than the current state of art technology as fresh water is used for tar removal. Speaking of environmentally friendliness, the gasifier is also producing ash as a waste. Therefore, further literature research is performed to answer the question of how coal gasification/combustion ash should be handled further the correct way. Proper handling of coal residues, such as gasification and combustion ashes will allow full protection of environment and the public health.

Coal ash is a residue resulting from gasification or from combustion, which consists of bottom ashes and fly ashes. The largest sources of world’s coal ash are from coal-fired power and heat production plants. Coal ash disposal either from coal combustion or gasification is a controversial topic as it is often debated that the coal ash from thermal processes (combustion/gasification) contains traces of heavy metals sourcing from the raw coal. By definition, trace elements refers to chemical elements that are present in a natural material at concentrations <0.1% wt or 1000 µg/g [97]. Coal is one of the main fuels in the energy sector of many countries. Utilization of coal for energy purpose results production of coal ash, commonly referred as CCPs (Coal Combustion Products). In 2010, it was estimated that in total 780 million tonnes of CCPs from the energy sector were produced world wide, which on average 53% of them were utilized further for various applications. Figures 30 and 31 below show the CCPs production and their utilization percentages of several countries. The statistical data corresponds to the year of 2010 [98]:

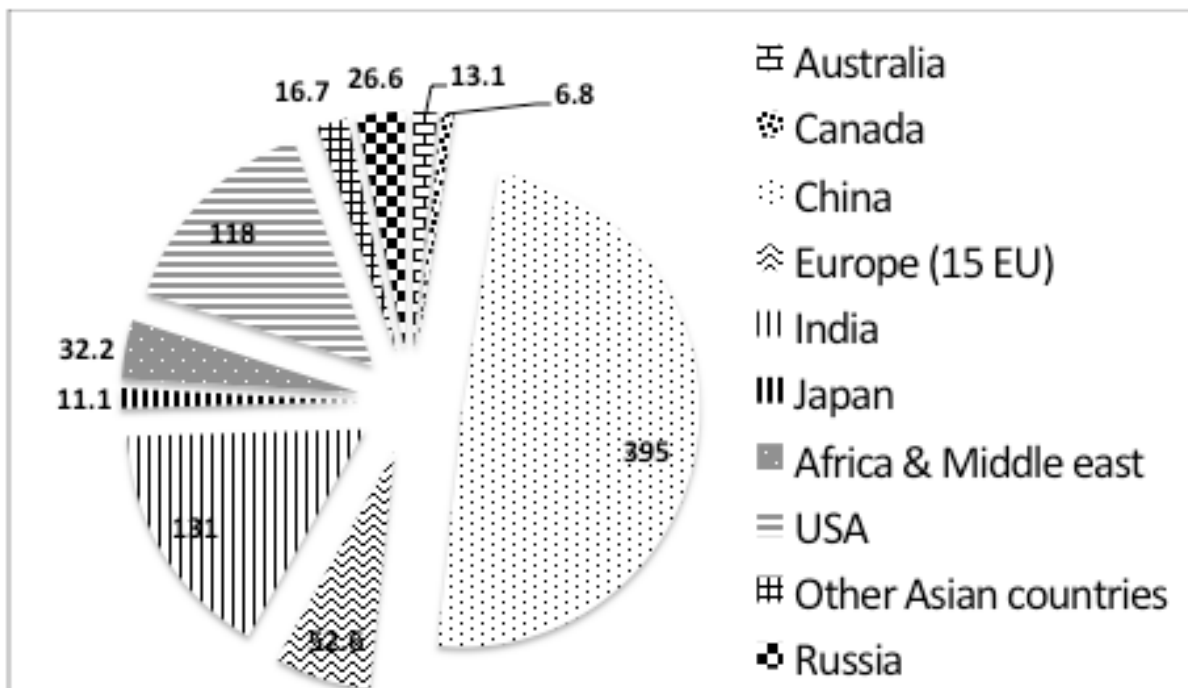


Figure 30: CCPs production statistics by country in 2010 (million tonnes) [98]

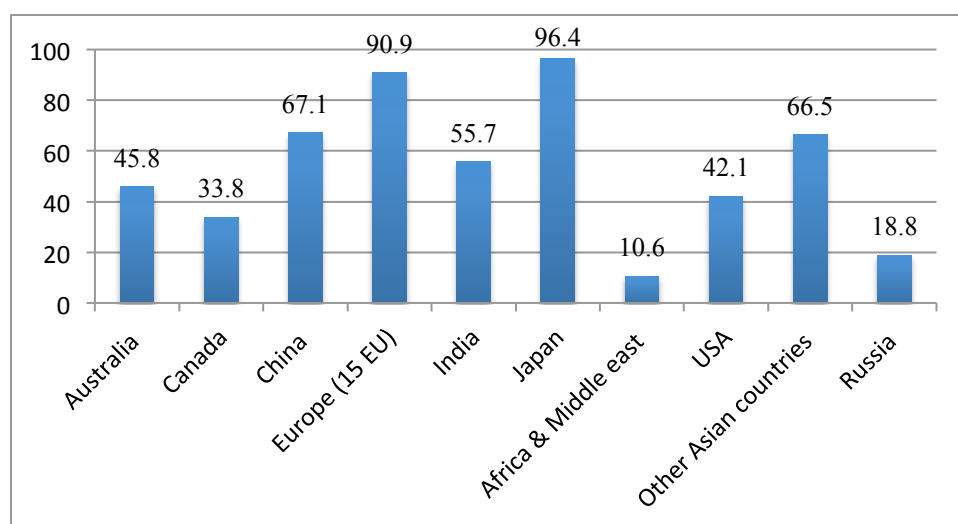


Figure 31: Coal ash utilization (%) by country in 2010 [98].

It can be seen from figure 31 above that the utilization of CCPs by country vary, highest being Japan (96.4%) and EU-15 (90.9%).

More detailed view on CCPs utilization trends within the European Union may be seen from the European Coal Combustion Products Association (ECOBA)’s statistical data. The production and utilization statistics reflect the common combustion products such as Fly ash (FA), Bottom ash (BA), Boiler slag (BS), Fluidized-bed-Combustion ash (FBC)-boilers, dry or wet de-sulphurisation products ash/products (spray dry absorption) and Flue Gas Desulphurization (FGD) gypsum. However, it should be noted that the given data from ECOBA statistics only reflect the situation in EU-15 member states and data from the other 13 member-states are not available. Moreover, ECOBA is working to implement data from the other members in their annual statistics. Due to missing production data, the CCPs production in EU-28 is presented as follows [99]:

Table 38: The coal ash production in E-28 member states [99]

	EU15	EU28*	EU*
Production	Million tonnes		
CCPs total	48.33	>105	>145
Ashes	37.69	>86	>124
De-sulphurisation product	10.64	>19	>21
Utilization rate			
Construction industry	52%	**	**
* Estimate based on coal consumption			
** Information on used only partly available			

It can be said that in year 2010, more than 145 million tonnes of CCPs were produced in Europe, of which 48 million tonnes were in EU-15. The figure below shows the CCPs production in the EU-15 member states between 1993-2012. Data after 2012 is not currently available.

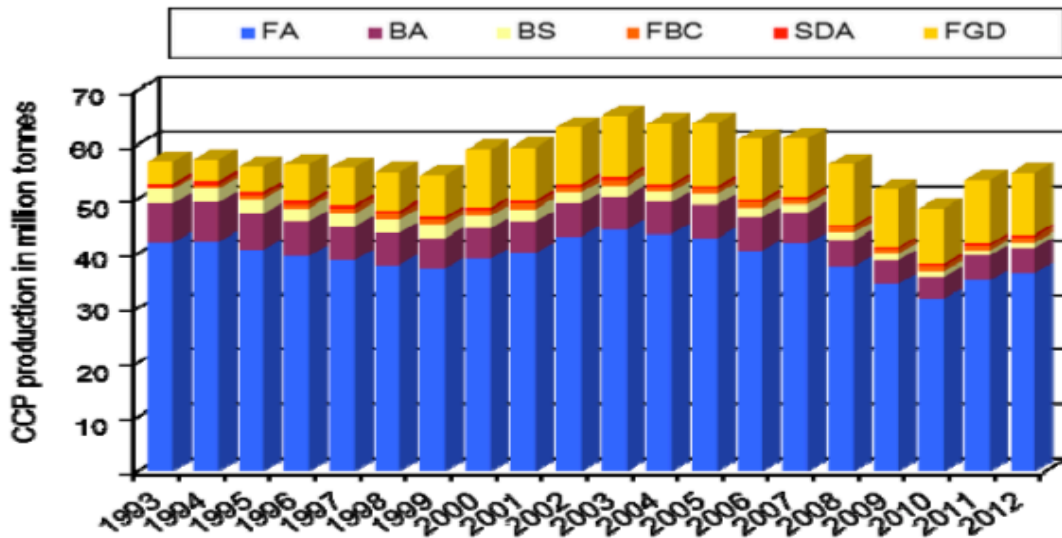


Figure 32: Coal Combustion Products (CCPs) development in EU-15 member states from 1993 to 2012 (FA-fly ash; BA-bottom ash; BS-boiler slag; FBC-Fluidized bed combustion’ SDA-spray dry absorption; FDG-flue gas desulphurization) [100].

Consequently, it can be seen from figure 32 above that the total amount of CCPs produced decreased from 57 million tonnes in 1993 to 55 million tonnes in 1999. Then the rise in production is seen in year of 2005, which rose up to 64 million tonnes. Such increase is explained by the fact that the electricity and heat generation from coal increased. Then starting from 2006, decrease in CCPs production is observed until year of 2010. Such decreased trend in EU-15 member states are due to less coal fed power and heat generation in some countries as a result of economic and industrial crisis in 2008. Moreover, political decision to reduce CO<sub>2</sub> and energies from renewables played an important role. However, because more coal based electricity and heat were generated in the other EU-13 member states, the total CCPs in EU-28 did not decrease.

In European countries, use of CCPs is established based on their long-term experience and due to increased knowledge of the CCPs technical and environmental benefits. CCPs is mainly utilized as a replacement for natural materials in building materials industry, civil engineering, road construction, for construction work in underground coal mining, as well as for re-cultivation and restoration purposes in open cast mines. As it was indicated earlier, degree of utilization CCPs in the EU-15 country is 91% and its breakdown is shown below on figure 33 [100]:

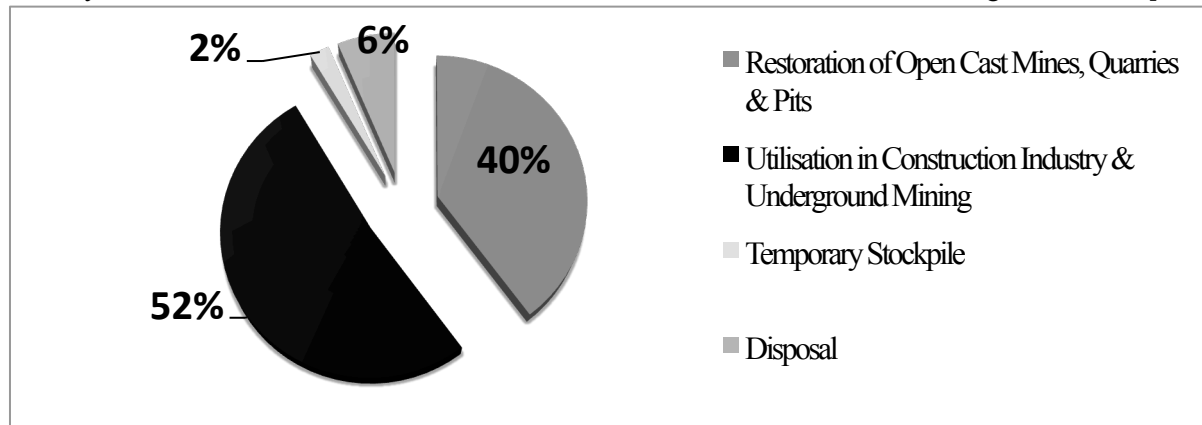


Figure 33: Utilization and disposal rate of CCPs in EU-15 in 2010 [100].



According to the above figure 33, about 6% of the total CCPs produced in EU-15 were disposed and rest was utilized. About 52% were used in construction industry, civil engineering and in under ground mining as construction material. 40% were used for restoration of open cast mines and pits. In addition, about 2% of the CCPs were temporary stockpiled for further use.

CCPs are determined to be suitable for above-mentioned purposes as it is available in huge amounts, available in long term, possess adequate product properties (grain size, distribution, surface), and have constant quality, meets the technical requirements and environmental compatibility. Use of CCPs allows saving of natural resources (mining, processing, transporting) reduces energy demand (mixing of fly ash for drying raw material) and reduces emission of CO<sub>2</sub> (0.7-1.2 kg/kg of clinker) in terms of construction material production by replacing certain fractions by CCPs.

Furthermore, utilization of CCPs is constrained by a number of factors. Some factors are political decisions, such as:

1. The Kyoto Protocol entered into force in 2005, agreed by 37 representatives of industrial countries in order to reduce the GreenHouse Gas emissions (GHG) to an average of 5% than that from the year of 1990 over the five-year period (2008-2012). Such protocol that is linked to the United Nations Framework Convention on Climate change encouraged the industrialized countries to stabilize their green house gas. This protocol has encourage the European countries to consume less coal, which leads to less available CCPs for utilization [101].
2. The Climate and Energy package (EU-20-20-20) entered into force in 2008 agreed by European Parliament and Council in order to reduce the GHG at least by 20% than the level of 1990, to increase the shares of the renewable energy to 20% and to improve the EU's energy efficiency by 20% by year of 2020. Moreover, Europe sees the potential to further reduce the emissions, which could be seen from its 2030 Energy and Climate policy framework proposal published in 2014. The commission proposed to cut the GHG emissions by 40% than the level of 1990 and increase the renewable energy share to 27%. European council targets to cut the emission of industrialized countries by 80-90% by 2050 [102].

Therefore, political decisions, directives and energy plans are leading to less available CCPs for utilization. Nevertheless, the benefits of using CCPs in construction industry have long been identified and have been accepted for construction materials by industries and authorities.

**5.2. FEASIBILITY OF TRACE ELEMENT EXTRACTION FROM CCPs**

Throughout the literature review on CCPs in Europe and their utilization, it was clear that use of CCPs as natural material replacement in construction and other industries has long been used. However, limited literature could be found on extraction of trace elements from the CCPs. Large scaled commercially operating plants for germanium extraction exists in China and Russia. For these commercial plants, the seam specifically enriched with germanium is mined and processed for germanium recovery. Moreover, there are also many commercially operating plants in China for aluminum extraction from highly enriched CCPs. However, extraction of other metals from coal ash are believed to be currently not profitable. Table 39 below shows example of industrial alumina plants in China [103]:

**Table 39: Commercial plants recovering alumina from coal ash in China [103]**

<b>Company</b>	<b>Location</b>	<b>Production capacity (million tonnes)</b>	<b>Status</b>	<b>Recovery technology</b>
Etuoke banner, Erdos	Inner-Mongolia Melic Sea Ordos Al Co., Ltd	Alumina 0.4	Started in 2013	Lime-Sinter followed by low-temperature Bayer process

Tuoketuo county, Hohhot city	Inner Mongolia dating International Recycling Resource Development Co., Ltd	Alumina 0.24, active calcium silicate 0.2	Started in 2012	Pre-desilication followed by lime-soda sinter
Tuoketuo county, Hohhot city	Inner Mongolia Datang International Recycling Resources Development Co., Ltd	Alumina 0.5, active calcium silicate 0.56, zeolite 4A 0.1	Started in 2015	Pre-desilication followed by lime-soda sinter
Zhungeer banner, Erdos	Inner Mongolia Datang International Recycling Resource Development Co. Ltd	Alumina 0.5, active calcium silicate 0.469	Started in 2015	Pre-desilication followed by lime-soda sinter
Zhungeer Banner, Erdos	Shenhua Group Co., Ltd	Alumina 1	Started in 2013	Acid leach
Zhungeer Banner, Erdos	Inner Mongolia Kaiyuan Ecological Aluminum Co., Ltd.	1 <sup>st</sup> phase: Alumina 0.4, Si-rich product 0.12 2 <sup>nd</sup> phase: Alumina 0.6, Si-rich product 0.18	2015/16	Ammonium sulfate sinter
Zhungeer Banner, Erdos	Huadian Inner Mongolia Energy Co., Ltd	Alumina 0.055	Started in 2013	Ammonium sulfate sinter
Etuoque banner, Erdos	Inner Mongolia Erdos Electrical Metallurgical Co., Ltd	Alumina 1, silica white 0.51, sodium silicate 0.77	2016	Acid leach followed by Bayer process
Qingshuihe county, Hohhot city	Inner-Mongolia Tongsheng electric Power Co., Ltd	Alumina 1	2016	Activation followed by water leach
Zhungeer banner, Erdos	Erdos qianhengxing Industrial Co., Ltd	First phase: Alumina 1.2	2013/2014	NA
Shuozhou city, Shanxi province	China Coal Pingshuo Coal Industry Co., Ltd	Alumina 0.1, silica white 0.04	2013	Pre-desilication followed by lime-soda sinter

It can be seen from above table 39 that recovery technologies vary and there are other commercial ventures that are developing different recovery technologies for metal recoveries from CCPs. Some examples of these ventures are shown below on table 40:

**Table 40: Metal extraction from coal ash technology developer examples [104]**

Company	Target metal
Elixsys	Aluminium, Trace metal concentrate
Emission Resource Group	Mg, Ti, Al, Rare-Earth-Elements (REE)
Expansion Energy	Ga, Ge, Ni, U, V, Fe, Zr and REE
Keystone Metals Recovery	Aluminum, Titanium, Iron and other trace elements
Latrobe Magnesium	Magnesium
Naval Research Laboratory	REEs
Orbite Aluminae	Aluminum, Scandium, Gallium
PSI Corp	REEs, Scandium, Yttrium
Rockton	REEs
Unicore	Germanium

Consequently, coal combustion residues are utilized as resources for strategic element recovery. This is the starting solution for environmentally sustainable disposal of CCPs. Furthermore, feasibility of extracting trace elements from CCPs remains uncertain, which following part looks at it closely.

During coal utilization, either through combustion or gasification, the trace elements are released from the coal. The amount of each trace element emitted depends on its concentration in the coal, its chemical and physical properties, thermal process parameters and lastly on particulate matter control devices utilized [105].

It is often debated that the waste ash from thermal processes hosts heavy metals, concentrated trace elements, and as such landfilling disposal methods should be avoided as they could leach out from the CCPs into the ground, which potentially could contaminate surface or ground water. This is specially the case if the original raw coal is rich in Hg, Cd, Pb, As, Cr and Tl. For example, within the European community, trace elements such as As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Sn, Tl and V are considered as elements of highest concern and their emission either through flue gas or through ash disposal are strictly regulated. In addition, U.S. Environmental Protection Agency (EPA) was requested to conduct investigation under the Clean Air Act Amendments of 1990 (Public Law 101-549) relating to 15 trace elements (antimony, arsenic, beryllium, cadmium, chlorine, chromium, cobalt, lead, manganese, mercury, nickel, potassium, selenium, thorium, and uranium) along with many other hazardous substances that are released into the atmosphere from the industries. Objective of the conducted study was to determine whether they were potentially hazardous and exposed health threats. These hazardous elements are collectively termed as “Hazardous Air Pollutants” or HAPs [106]. They are known or suspected of causing cancer or other serious health implications.

Therefore, more literature review is conducted to get more insights on what trace elements are found in coal, modes of trace element occurrence and which of the trace elements are expected to be found in the coal gasification ash (CGPs). Hence, determining how much of trace elements can be extracted and defining whether marketing of CGPs for trace elements extraction is subject to EU REACH regulation. Extraction of trace elements from CGPs may limit some of the expenses and environmental hazards associated with ash disposal.

### **5.2.1. TRACE ELEMENTS IN RAW COAL**

Enrichment of the trace elements in coal is affected by many geological factors and by the forming periods. There are different types of coals and they vary by differing contents of organic and inorganic (mineral) components, sulfur and ash. Long utilization of coal has allowed broad knowledge of various problems that accompany use of coal. For example, the landfilled coal ash may adversely affect the quality of the surface and ground water. Use of coal for various purposes may emit higher or lower amounts of trace elements that could be considered hazardous and this range in property results from coal's diverse origins, which includes the long and complex geologic histories of the coal deposit.

Coal consists of complex organic and inorganic compounds. For example, there are approximately more than 120 inorganic compounds already identified in coal. Their sources could be either from the swamp from waterborne or windborne sediment or from the elements in the original vegetation. Out of 120 different minerals identified, 33 of them occur in most coals, of which only 8 of them are abundantly found in coal and considered as the major constituent of the coal. These abundantly found minerals, as well as other minerals found in coal are shown below on table 41 [107]:

Table 41: Common minerals in coal and their elemental compositions [106,107]

Mineral name	Chemical Composition	Comment	
Quartz	SiO <sub>2</sub>		<i>Major mineral constituent. In order of abundance.</i>
Clay Minerals:			
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	May have Mn. Clay main contain Be, Cr, Ni and other trace elements	
Illite	KAl <sub>4</sub> (AlSi <sub>7</sub> O <sub>20</sub> )(OH) <sub>4</sub>		
Montmorillonite	(1/2Ca,Na) <sub>0.7</sub> (Al,Mg,Fe) <sub>4</sub> [(Si,Al) <sub>4</sub> O <sub>10</sub> ] <sub>2</sub> (OH) <sub>4</sub> · nH <sub>2</sub> O		
Chlorite	(Mg,Al,Fe) <sub>12</sub> [(Si,Al) <sub>8</sub> O <sub>20</sub> ](OH) <sub>16</sub>		
Pyrite	FeS <sub>2</sub>	May contain As, Cd, Co, Hg, Ni, Sb and Se	<i>Minor mineral constituent.</i>
Calcite	CaCO <sub>3</sub>		
Siderite	FeCO <sub>3</sub>	May contain Mn	
Analcime	NaAlSi <sub>2</sub> O <sub>6</sub> ·H <sub>2</sub> O		
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH,F,Cl)		
Barite	BaSO <sub>4</sub>		
Chalcopyrite	CuFeS <sub>2</sub>		
Clausthalite	PbS		
Crandallite Group			
Crandallite Florencite Gorceixite Goyazite	CaAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> · H <sub>2</sub> O CeAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> BaAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> · H <sub>2</sub> O SrAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> · H <sub>2</sub> O		
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>		
Feldspars	(Ca,K,Na)AlSi <sub>3</sub> O <sub>8</sub>		
Galena	PbS		
Marcasite	FeS <sub>2</sub>	May contain As, Cd, Co, Hg, Ni, Sb and Se	
Monazite	(Ce,La,Y,Th,Nd)PO <sub>4</sub>		
Rutile/Anatase	TiO <sub>2</sub>		
Sphalerite	ZnS	May contain Cd	
Xenotime	YPO <sub>4</sub>		
Zircon	Zr[SiO <sub>4</sub> ]		
Chromite	FeCr <sub>2</sub> O <sub>4</sub>		<i>Trace mineral constituent.</i>
Gibbsite	Al(OH) <sub>3</sub>		
Gold	Au		
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O		
Halite	NaCl		
Magnetite	Fe <sub>3</sub> O <sub>4</sub>		
Muscovite	KAl <sub>2</sub> (AlSi <sub>3</sub> O <sub>10</sub> )(OH) <sub>2</sub>		

It can be seen from table 41 above that only 8 minerals (quartz, kaolinite, illite, montmorillonite, chlorite, pyrite, calcite and siderite) are abundantly found and are considered as the major mineral constituent. These major minerals in coal are made up of common elements of oxygen, aluminum, silicon, iron, sulfur and calcium. These minerals in coal contain bulk of trace elements present in coal.

Minerals in coal occur as single crystals or cluster of crystals intermixed with the organic matter or fill void spaces in coal [107]. Mineral content of the coal vary from seam to seams and even differ within the same seams. Coal mineral matters can be classified as inherent (organic) or adventitious (inorganic) mineral matters. Coal's inherent mineral matters are closely associated that the substances cannot be easily removed from the mineral matter. In contrast, the adventitious mineral matter is inorganic materials that are less loosely associated with the coal and separation of the substances from the mineral matter is done easily. It is also common to divide the coal minerals into five main groups: silicates, sulphide and sulphate minerals, carbonates and other minerals.

**Silicate Minerals:** Silicate minerals take up of about 60-90% of the total mineral matters in most bituminous type coals and often occur as aluminosilicates (clays) and quartz [108]. Trace elements such as Cr and V are associated with clay. Commonly found clay type across the world coal is kaolinite, followed by quartz.

**Sulphide Minerals:** The most commonly found sulphide minerals associated with coal are pyrite ( $\text{FeS}_2$ ) and Marcasite ( $\text{FeS}_2$ ). Although they have same chemical formula, their crystal structures differ from one another. For example pyrite has isometric crystal structure, while marcasite has orthorhombic. Commonly encountered coal processing problems, such as boiler tube fouling or corrossions are caused by the sulphur content in the coal, which sulphide minerals contribute to coal sulphur content. When sulphide minerals go through thermal processes, they get broken down to Fe and S. Then they react further with  $\text{O}_2$  to become Iron oxide and a gas  $\text{SO}_x$ . Therefore, they partition to the coal ash (heavy solid) and to flue gas respectively [107]. Trace elements such as Cd, Co, Ni can be found in the sulphide minerals.

**Sulphate Minerals:** Sulphate minerals are often found in oxidized coal and are not significantly present in un-oxidized coal. The sulphate gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and Barite ( $\text{Ba}_2\text{SO}_4$ ) are often found in fresh coal. In oxidized coal, pyrites are oxidized to give hydrated states of ferrous and ferric sulphates ( $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ ). Trace elements such as Cr, Mn, Mo or Ni can be found in coals with sulphate minerals [109].

**Carbonate Minerals:** The major cations of coal carbonate minerals are calcium, iron and magnesium. Carbonate minerals usually take up about 10% of the total minerals found in coal. Most common carbonate minerals found in coal are Calcite ( $\text{CaCO}_3$ ), Ankerite (mixed crystals of Ca, Mg and Fe carbonate) and Siderite ( $\text{FeCO}_3$ ). Abundance of these minerals in coal varies from coal to coal [109].

Modes of occurrence of trace elements refer to how the trace elements are chemically bonded to its organic/inorganic compounds and how they are physically distributed in the coal [110]. If the trace elements mode of occurrence is known, it helps to determine how the trace elements would behave when coal goes under thermal processes, cleaning and leaching. Such that appropriate measures can be taken to recover the valuable elements or to capture the toxic trace elements before it gets vented to the atmosphere.

According to Raask et al [108], trace elements mode of occurrence and their distribution in coal and in the mineral matters change depending on the chemical characteristic of the elements and coal quality. For example, the trace elements could be associated either with organic or inorganic matters or with both with varying proportions with coals globally. However, literature on trace elements mode of occurrence is very limited, hence there is no solid general rule or trend that could be utilized to predict elemental modes of occurrence in coal. Various investigation studies were conducted to determine such general rule, but gave wide variation of elemental modes of occurrence with various degrees of success. Therefore, it

is difficult to determine how each trace element occurs and it becomes even harder if its concentrations is less than 100 ppm. Table 42 below shows likely modes of occurrence for some trace elements determined by Finkelman et al [111], with level of confidence. The higher the number (8), the higher the level of confidence and lower the number (1), lower level of confidence[111].

**Table 42: Traces elements mode of occurrence probability in coal [110]**

Elements	Modes of occurrence	Level of confidence
Antimony	Pyrite and accessory sulphides	4
Arsenic	Pyrite	8
Beryllium	Organic association	4
Boron	Organic association	6
Cadmium	Sphalerite	8
Chromium	Organic or clay association	2
Cobalt	Pyrite, Some in accessory sulphides	4
Copper	Chalcopyrite	8
Lead	Galena	8
Mercury	Pyrite, carbonates	6
Manganese	Ankerite	8
Molybdenum	Sulphides	2
Nickel	Unclear	2
Selenium	Organic association, pyrite and accessory Sulphides, selenides	8
Uranium	Organic and Some in Zircon	7
Vanadium	Clays and Organic association	3

Out of 92 naturally occurring elements in the periodic table, 76 of them can be found in coal. However, most of them are usually present in trace amounts. Sometimes, the traces elements (silver, zinc, or germanium) can be found concentrated in a specific coal bed, which the bed becomes valuable for element extraction [112]. Inorganically bound traces elements, especially those associated with clays or pyrates could be removed from the coal by cleaning process (crushing or washing).

On the other hand, the organic compounds of the coal consist of elements carbon, hydrogen, oxygen, nitrogen, sulfur and traces amount of various few elements. However, elements that are bound to the organic part of the coal are extremely complex and are not well understood. Removal of trace elements from coal by cleaning processes (crushing or washing) is very difficult if the intended trace elements have affinity for organic compounds of the coal. They can only be removed as a result of burning (combustion or gasification) the coal or by deep chemical leaching. These organically bound trace element removal methods are often considered very difficult and expensive procedure [105].

Depending on whether the traces elements of interest has affinity for organic or inorganic compounds of the coal, efficient extraction method could be applied, such that the trace elements can be recovered and put to some other uses. The affinities of the trace elements affect quality of the coal. However, as of today only various forms of ash, small amounts of germanium and aluminum are extracted from coal [107]. Although much is known regarding the mineral components in coal, much remains uncertain regarding their occurrence, abundance, origin and compositions. For example, type of clay mineral in a coal (montmorillonite or illite) determines how the coal will react when coal is put under thermal process. Montmorillonite for example might or might not dissociate into its constituent parts under thermal process. If it does breakdown, then its constituent parts may recombine with other elements or other available minerals during cooling. Such recombination results minerals depositions on inner walls of the furnace or boilers. This process is often referred as fouling



or slagging and this adversely affects the heat exchangers, which in the end results loss of efficiency or even break down, which leads to costly repair or maintenance [107]. Table 43 below shows average values of various trace elements in coals originating from China, South Africa and the Global average value.

**Table 43: Trace elements average values of China, South-Africa and global average [113-115]**

Element (ppm)	Mean values China	Mean South-Africa values	Average global values
As	3.78	3.70	9.80
Cd	0.25	0.41	0.23
Co	7.08	8.50	6.20
Cr	15.14	55.2	18.0
Cu	17.50	14.2	18.0
Hg	-	0.20	0.11
Mo	-	3.15	2.10
Mn	116.2	107.5	82.0
Ni	13.7	20.0	17.0
Pb	15.1	9.60	9.90
Sb	-	0.20	1.09
Se	-	1.23	1.50
V	35.1	35.1	30.0
Zn	41.4	-	23.0

It can be seen from table 43 above that the trace element concentrations in global coal varies from country to country. Because the objective of this literature research is to assess compatibility of EU REACH regulation for trace element extraction from CCPS or CGPs, the global average values for trace elements are sufficient to determine whether trace elements extraction from CGPs is subject to REACH regulation. Therefore, for any further consideration, the global average values for the trace elements in coal will be considered.

**5.2.2. PARTITIONING FATE OF TRACE ELEMENTS IN FIXED-BED GASIFIER**

When coal is put under thermal process, either combustion or gasification, it undergoes complex changes, such as thermal decomposition, fusion, disintegration, agglomeration, char formation and volatilization of trace elements. At the same time, the mineral content of the coal also under goes complex changes resulting slag, flash or bottom ashes. It is common to classify the trace elements based on what is known as relative trace element enrichment factor (RE) . The RE in the coal ash is defined as [116]:

$$RE = \frac{\text{Trace element in ash}}{\text{Trace element in coal}} * \frac{\% \text{ ash in coal}}{100}$$

The trace elements classification based on enrichment concept is divided into following 3 classes:

**Class 1:** For this class, the RE~1 and the trace elements get enriched in the bottom and fly ashes. Therefore, efficient control of particulate emission is directly related to release of trace elements belonging to this class, which includes for example Mn, Be, Co and Cr

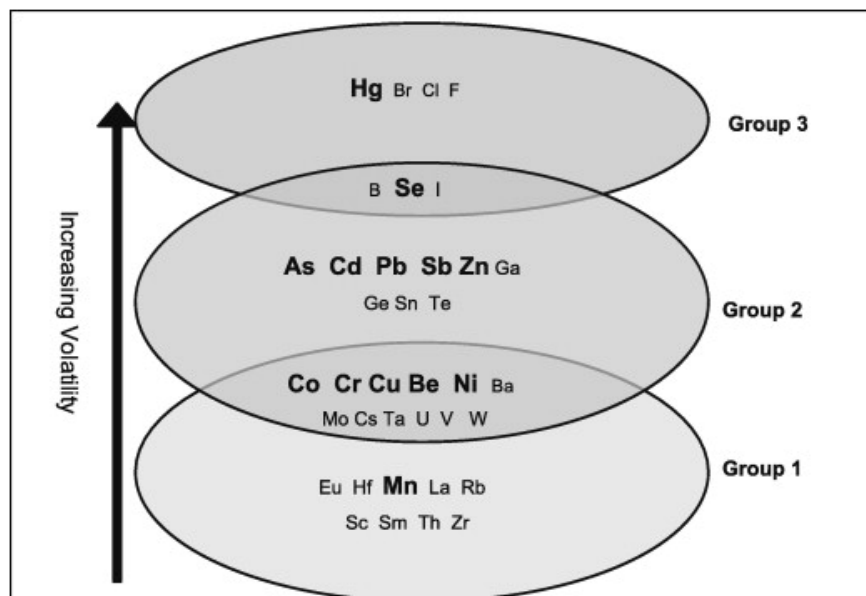
**Class 2:** For this class, the RE<0.7 for bottom ashes and ~1.3-4 for fly ashes. Trace elements belonging to this class are volatilized in the boiler or gasifier and get condensed downstream. Many studies have indicated that class 2 trace elements get concentrated in the fly ash (finer particles) and enrichment in fly ash increases with decreasing particle size of the fly ash. This is because upon cooling of the flue gas, the volatile elements have tendency to condense on surfaces of smaller particles of the flue gas. Therefore, again the particulate matter emission

control measures are in charge of collecting these fine particles containing condensed trace elements. Class 2 elements include As, Cd, Pb and Sb.

**Class 3:** For this class, the  $RE \ll 1$  for bottom ash and  $RE \gg 10$  for fly ash. The most volatile elements belong to this class and are not enriched in solid phases like in the bottom and fly ashes. These volatile elements remain in the gas phase and capturing of them is dependent on particulate control. In some cases, the particulate controls fail to capture very volatile elements such as Hg.

Since objective of this part has focus on fixed-bed gasifier ash, trace element partitioning in fixed-bed gasification process should be closely looked at, which following part covers it.

**Fixed-bed gasifier:** As a start to get better understanding of partitioning behavior of trace elements in fixed-bed gasification process, the trace elements in the raw coal are divided into three classifications according to their volatility and volatility behavior of their simple compounds (oxide, sulphides and Chlorides) as shown below on figure 34 [117, 118]:



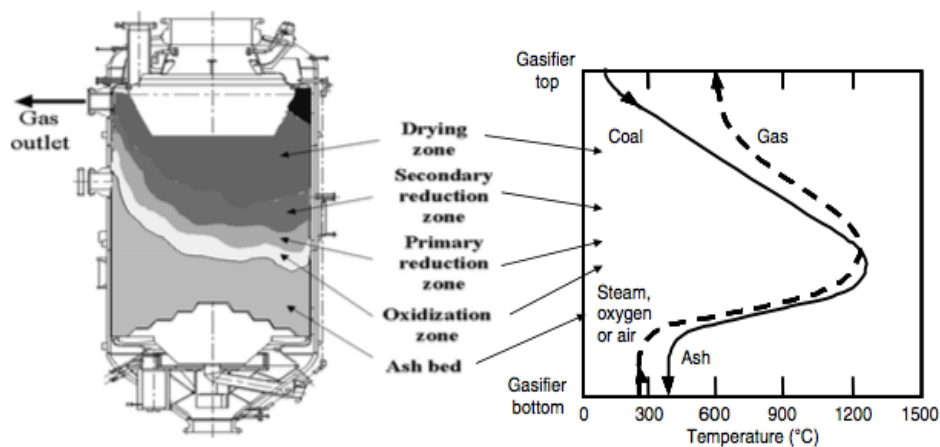
**Figure 34: Trace element classification based on their volatility behavior [117, 118]**

According to the trace elements volatility classifications, the trace elements in group 1 are the least volatile and are expected to remain in the gasification ash. The trace elements in group 2 are more volatile and they can partition between the ash and the gaseous phase, where the vaporized species get condensed on the ash particle as the ash cools. Trace elements belonging to group 3 are highly volatile (low boiling point) and show little or even no tendency to condense from the vapor phase. The trace element classification of Erickson et al [118], is disagreed by other researchers who are working within this topic as there are some elements that have shown intermediate behavior, which leads them to be placed in more than one group in the classification. The 11 trace metals that are emphasized (in bold) except Cu and Zn are considered to be HAPs, which are known or suspected of causing cancer or other serious health implications.

Many researchers conducted investigation work in order to understand the partitioning behavior of trace elements in gasification process for the highly complicated volatile trace elements.

1. **Entrained flow gasification:** Helble studied the partitioning behavior of As, Cr, Hg, Pb, Se and Zn between vapor and condensed phases as a function of temperature increase with varied pressure from 1 to 20 atm for entrained flow gasification of Illinois No.6 type coal. The result indicated that elements Hg and Se will remain mainly in the vapor phase throughout an Integrated combined cycle (IGCC) power cycle, while the other elements would partition to either particulate solid, heat transfer surfaces or to the aqueous streams[119].
2. **Fluidized bed gasification:** Study conducted by Reed evaluated the formation of simple salts (chloride, oxides, sulphides) and pure condensed phases in air-blown pressurized fluidized bed gasification on British coal. It was found that most trace elements could be removed from the gasification products (fuel gas, syngas), except Hg, Se, As and Cd [120].
3. **Underground gasification:** Thermodynamic equilibrium studies of trace element transformation during underground gasification of Chinese coal were conducted [121]. It was found that Se was the most volatile trace element, found in forms of  $H_2Se(g)$  in the gas phase. In addition, trace elements As, Pb, Cd and Sb were determined to be volatile, but not to the same degree as Se. These volatile compounds were found to evaporate at low temperature and occurred in gas phase as As (g),  $SbCl(g)$ , Cd (g) and  $PbS(g)$ . However, they were condensed and enriched in the ash when gasification gas cleaning processes were applied. Study had found that the partitioning behavior of trace elements such as As, Se, Sb were affected by the gasification pressure, for example high pressure would lead to hydrides of these trace elements.

The literature data regarding trace elements partitioning behavior in coal gasification is not widely available as it is the case for the conventional boiler for coal combustion. However, there is abundant information from thermodynamic equilibrium modeling studies, pilot/bench scaled units and commercial scaled IGCC plants [122]. The thermodynamic modeling studies indicate different volatility behavior of trace elements in coal gasification at different parts of the gasifier. For example, trace elements are more volatile at the reducing condition than the oxidizing environment of the gasifier, possibly due to volatile gaseous compounds (chloride, sulphides and hydroxides) are more stable in reducing condition. However in the oxidizing condition, the trace elements have higher tendency to be converted into less volatile compounds (oxides and sulphates). Figure 35 below demonstrates the typical reaction zones in the Sasol-Lurgi MK IV Fixed-bed-dry-bottom gasifier with respect to the temperature profile:



*Figure 35: Reaction zones in Sasol\_Lurgi fixed-bed-dry-bottom gasification process with respect to the temperature profile [123].*

In regard to trace elements partitioning behavior in fixed-bed type coal gasifier, Bund and Waanders et al [123, 125], from Sasol Technology Ltd and School of Chemical and Minerals Engineering, North West-University in South Africa conducted the study. The study involved utilization of theoretical Fact-Sage 5.3 modeling program as modeling tool to predict the volatility behavior of trace metals of South-African Secunda lump coal gasified in Sasol-Lurgi MJ IV FBDB gasifier. The modeling software allows calculation at high temperature and handles all phases of the involved materials [124]. The prediction results from such modeling package often matches to the reality results. However, such model was never tested to fixed-bed type gasifier operating on lump coal. The predicted results from the thermodynamic models are based on aqueous solution chemistry and might not work for gasifiers operating with lump coal as the chemical environment is vastly different. The result of this prediction was compared against the actual plant profile result from a quenched and sampled commercial-scale fixed-bed gasifier. The studies were conducted in two parts, in which the first part focused on volatile elements such as Hg, As, Se, Cd and Pb. The second part focused on semi-volatile trace elements such as Cu, Mo, Ni and Zn.

The prediction data from the model for the volatile trace elements corresponded to that from the actual measurements, except for As. As predicted, it was found that trace elements Hg, Cd, Pb, As and Se are highly volatile and partitioned into the gas phase. In particular Hg amongst them were the most volatile element during fixed-bed gasification and was found in gas phase in form of elemental Hg(g). The volatility of these elements follows the order [123]:



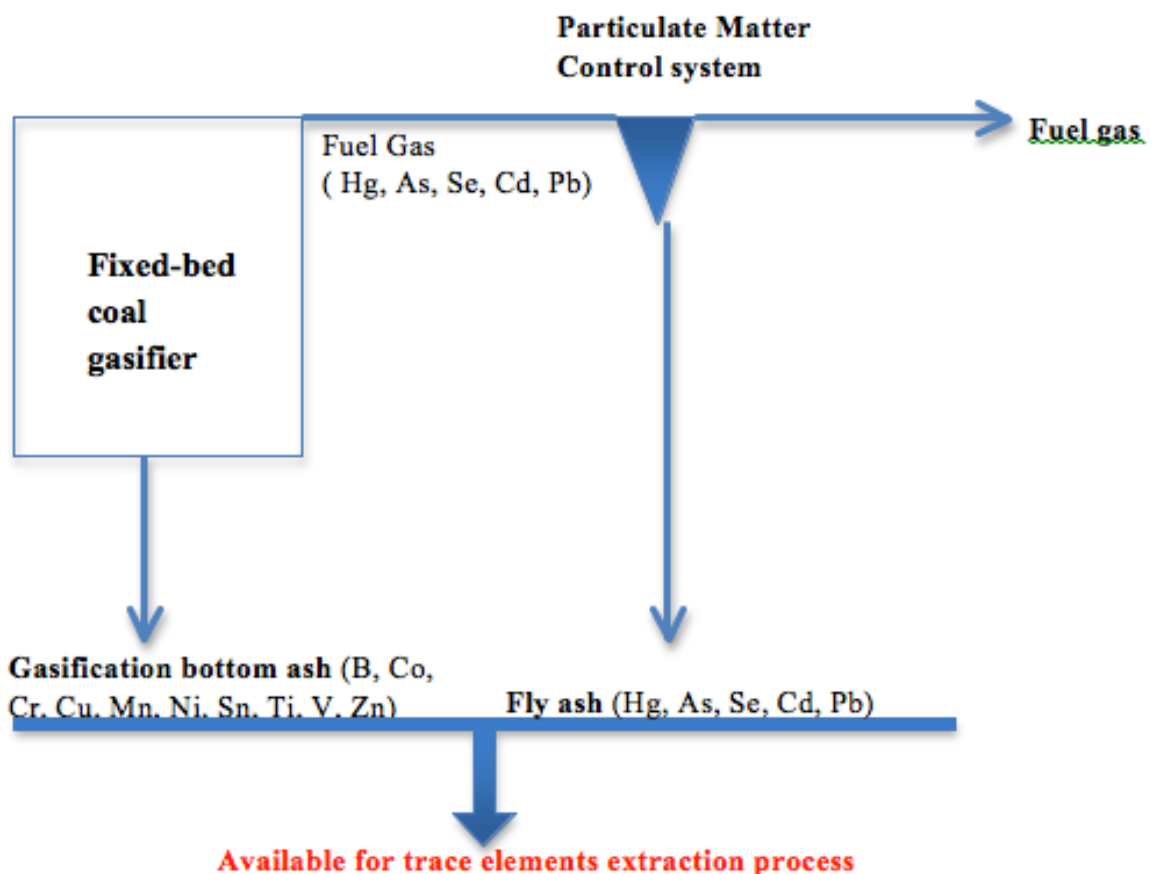
In addition, the speciation prediction showed that species of Hg, AsH<sub>3</sub>, H<sub>2</sub>Se, PbSe, Cd, CdS and PbS/Pb/PbCl could potentially exist in the raw gas phase. This allows to select the most efficient raw gas treatment options downstream of the gasifier.

The second part of the Fact-Sage thermodynamic modeling focused on the semi-volatile trace elements such as Cu, Mo, Ni and Zn [125]. These elements showed limited de-volatilization behavior in the drying and pyrolysis zone of the gasifier. Moreover, in the reducing zone of the gasifier, they are highly volatile resulting gaseous species with increasing temperature. The degree of volatility in the reducing zone are in order of Zn > Mo > Cu > Ni. However, such result is opposite of the experiment results and this is possibly indicating that the thermodynamic equilibrium conditions do not prevail in a fixed-bed gasifier operating on lump coal. This is because in reality mass and heat transfer limitations across coarse coal particles apply and the reactions are kinetically limited. In addition, the study had found over-balance for Mo (165%) and Ni (550%). This over balance was tried to be correlated to the gasifier ash grate ploughs, which contain composite Ni/Cr rich alloy. However, erosion of the ash grate plough should maximum contribute 2% for the over balance. Thus, it is assumed that there was external contamination or chemicals accumulation during sampling of the gasifier and more attention should be paid for the further studies.

Furthermore, Hlatshwaya and Wagner et al [126], performed trace elements mass balance of coal, ash, coal tar, gas-liquid and limited raw gas samples from commercial-scaled test that was being conducted at a Sasol-Lurgi fixed-bed gasification plant located in South-Africa. The conducted study had given that volatile trace elements such as Hg, As, Se, Cd and Pb were found in the raw gas, while the other trace elements had partitioned to the ash. The trace elements of South-African coals were associated to the inorganic (pyritic sulphur-sulphide form) parts of the coal [126].

The Fact-Sage equilibrium model used in these studies was found to be useful in order to predict which trace elements can be thermodynamically attained. However, it is said that pure-equilibrium model has its drawbacks as for example the carbon conversion is often controlled by non-equilibrium factors.

Therefore, based on the literature review covered in this part, it can be said that the volatile elements such as Hg, As, Se, Cd and Pb are partitioned into the raw gas from the coal gasification process and remainder non-volatile elements are partitioned into the coal ash. Because the objective of this part is to perform compatibility assessment of EU REACH regulation for trace elements extraction from coal gasification ash, no further effort is paid regarding the trace element partitioning in fixed-bed coal gasification. Now that which trace elements are partitioned into coal gasification ash, the next step would be to match possible recovery technology for each corresponding trace elements of interest. However, such recovery technologies will not be covered. For selecting the recovery technologies, it is important to know the speciation variation of each trace element in the coal ash. Again there is not solid rule that could help to predict speciation variation of trace elements in the ash as coals from different location vary in composition and their compositional changes will behave differently resulting variation of speciation variation.



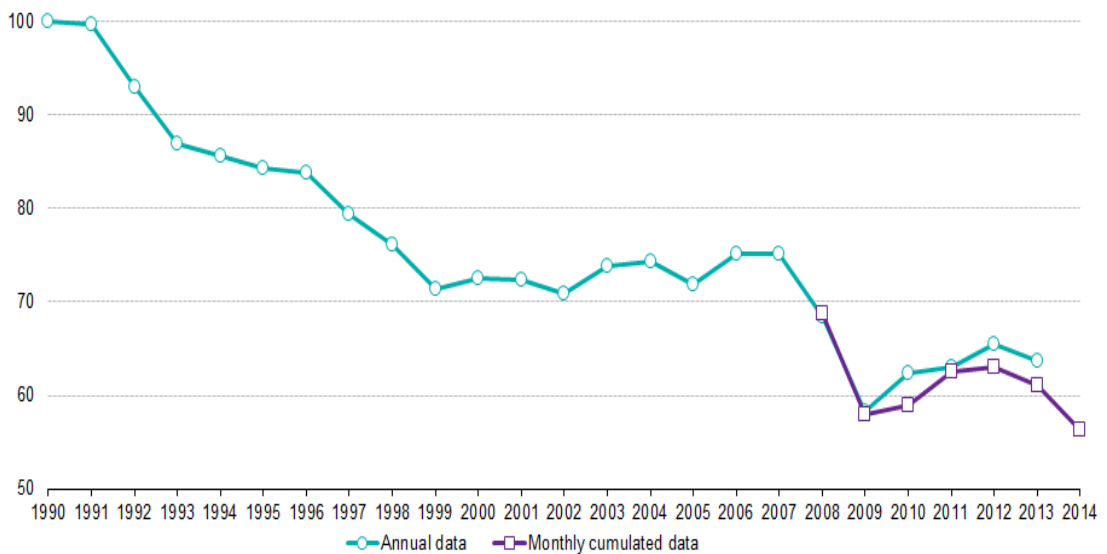
*Figure 36: Trace elements partitioning path summary in Fixed-bed type coal gasifier*

Furthermore, investigations on speciation variation of trace elements in coal gasification and coal combustion has shown that trace elements recovery from gasification is more environmentally benign process and is more advantageous for mitigating the risk of trace elements pollution from coal ash in the environment than coal direct combustion ash. According to Hui and Xiaoyi et al [127], a study on speciation variation of trace elements in

coal gasification and combustion, it was found that the trace elements are changed partly from the active (liable) fraction to the residual (non-labile) fraction in the gasification and combustion processes. The trace elements bound to the active fraction in gasification ash are diminished in the process of brown coal gasification more than in the conventional combustion of brown coal. Therefore, since trace element recovery from coal ash is a very complex process, which requires many chemical substances suitable for each speciation of each trace element, gasification ash is more appealing than conventional combustion ash due to reduced speciation variation [127].

**5.2.3. QUANTIFICATION OF TRACE ELEMENTS IN COAL ASH**

The conducted literature research on trace elements partitioning in fixed-bed gasification process has indicated that the volatile trace elements (Hg, As, Se, Cd, Pb) would partition into the gas phase and will partition into the flash ash only if the utilized particulate matter filter system is efficient enough to capture them. The other semi and non-volatile trace elements will partition into the gasifier bottom ash. Quantification of each trace element in coal ash available for extraction is at of interest due to the set objective. Therefore, this part covers coal consumption trend in EU-28 countries and quantifies how much of what trace elements are available from annually consumed coal in EU-28. Figure 37 below demonstrates the hard coal consumption trend in EU-28 starting from 1990 until 2014.



**Figure 37: Hard coal consumption in EU-28 between 1990-2014 (1990=100%) [128].**

According to figure 37, the hard coal consumption in EU-28 decreased from year 1990 until 1999. Then between 1999-2007, decrease of hard coal consumption remained relatively stable (between 360-380 million tonnes), followed by further decrease in consumption between 2008-2009. In 2014, the hard coal consumption reached its lowest level at 285 million tonnes and this corresponds to 56% of the total coal that was consumed back in 1990.

The latest hard coal consumption data in EU-28 is from 2014 and the consumption data for 2015 is expected to be published in June 2016. Therefore, for trace elements quantification, data corresponding to year 2014 and world average trace element amounts in coal are utilized. The table below demonstrates how much of each trace elements can be extracted from the 285 million tonnes of hard coal consumed annually:



*Table 44: Trace elements quantifications*

	<b>World Average (µg/g)</b>	<b>Tone/Year EU-28</b>
As	9.8	2793
Cd	0.2	65.55
Co	6.2	1767
Cr	18.0	5130
Cu	18.0	5130
Hg	0.1	31.35
Mo	2.1	598.5
Mn	82.0	23370
Ni	17.0	4845
Pb	9.9	2821.5
Sb	1.1	310.65
Se	1.5	427.5
V	30.0	8550
Zn	23.0	6555

The table 44 above shows available trace elements from hard coal combusted ashes in EU-28 in 2014 (285 million tonnes). It should be noted that quantified amounts are possible available trace elements if all the coal ash were solely utilized to recover the trace elements. However, in reality it has shown that EU-28 countries have high percentage for coal ash utilization for various applications, which will lower full recovery of trace elements. Even then, it can be seen that extraction of trace element via ash recovery process, the amount is more than 1 tone per year.

Furthermore, above quantification is from the coal combustion ash and not from coal gasification ash. Coal in EU-28 is consumed for the purpose of power generation. Electricity and heat production via coal gasification and fuel gas in EU-28 are not common practice. However, if EU-28 were to gasify same amount of coal instead of directly burning, the available trace elements from coal gasification ash will remain the same as indicated on table 45 above. If such shift is thought to be unrealistic, then EU-28 still has CCPs for trace element extraction.

### **5.3. COAL COMBUSTION/GASIFICATION ASH REGULATION**

The previous parts have indicated majority of the available trace elements will partition either to gasifier bottom or flash ash, hence available for recovery. It has also shown that potential to recover trace elements from annually consumed coal is more than 1 tonne. If CCPs were marketed on European market for trace element recovery, they would subject to EU REACH regulation. On the other hand, CCPs can also be subject to waste directives. Therefore, this parts focuses on relating European regulations in the case where trace elements are recovered from the annually produced CCPs.

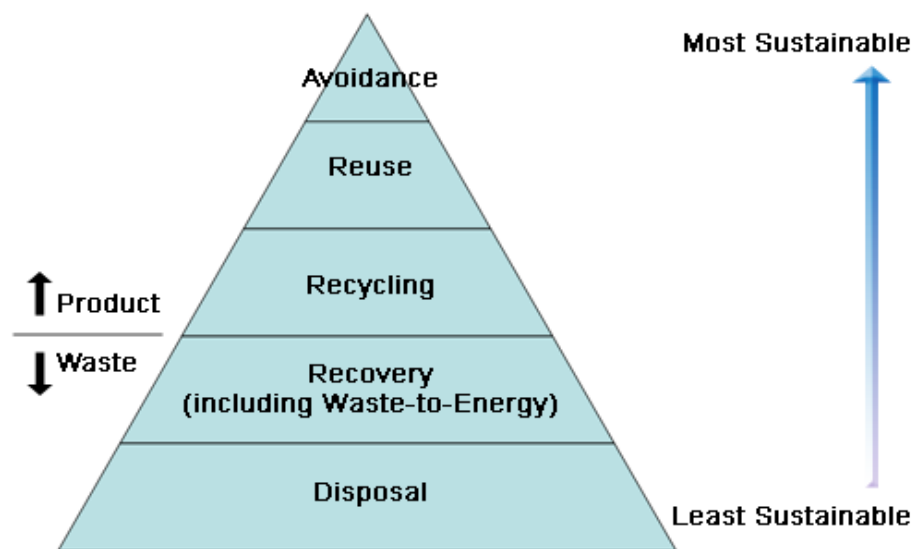
#### **5.3.1. WASTE DIRECTIVE**

Currently, there is no international regulation or documentation except the Basel Convention (Control of trans boundary movement of hazardous waste and their Disposals) relating to coal handling issues. Each country has their own national legislations that handle issues accompanying coal usage. Depending on their legislation, CCPs are assigned status of either wastes or non-wastes.

In addition, there is no common legal definition of ash in different countries and this is leading to confusion of whether CCPs is waste or product or recycled materials. Currently, the members of the World Wide Coal Combustion Product Network (WWCCPN) are trying to

develop a common CCPs terminology, which covers CCPs resulting from coal combustion and from other solid fuels [129].

The European waste Directive 2008/98/EC sets out the clear definition of waste, recycling and recovery. It also reflects basic waste management principles that the wastes should be managed without endangering human health and the environment. In particular, risk to water, air, soil, plants and animals. The waste legislation and the policy of the EU member states shall apply as a priority order the following waste management hierarchy:



*Figure 38: Waste hierarchy in the EU Directive 2008/98/EC [130]*

According to the above shown waste hierarchy, it shows that the European member states must avoid or prevent waste generation and is considered as the most preferred option. The least preferred option is disposal and is considered as the least sustainable. The legislation considers energy efficient waste incineration a recovery operation, a provision that facilitates resource efficiency, which ultimately means reduced use of fossil fuel. According to the European waste directive (Directive 2008/98/EC) dating 19<sup>th</sup> November, it is stated [131].

*There should be no confusion between the various aspects of the waste definition and appropriate procedures should be applied, where necessary, to by-products that are not waste, on the one hand, or to waste that ceases to be waste, on the other hand*

This directive has further specified certain aspects of the definition of waste, indicating clearly what becomes waste, or product or end-of waste products.

**By product:** Article 5 of the above stated directive outlines the conditions for being by-product. Substance or object, resulted from a production process, which the primary aim is not the production of that item, may be regarded as being not waste, but as being by-product only if following conditions are met:

- Further use of substance or object is certain
- Substance or object is directly used in intended application without any further processing other than normal industrial practice
- Substance or object is produced as integral part of the production
- Further use is lawful, meaning substance or object meets all relevant product, environmental and health protection requirements for the intended application. Use of

substance or object does not pose adverse effect to environment and to the public health

The above points are the basic conditions and measures may be adopted to determine the criteria to be met for specific substance or objects that are to be regarded as by-product. Therefore, if coal combustion ash from power plants or coal gasification plants are to be used directly, then coal ash ceases to be considered waste and is instead regarded as by-product as it fulfills the conditions outlined in Article 5 of the directive..

**End-of-Waste products:** Pre-conditions for CCPs being regarded as “End-of-Waste” products are outlined in the Article 6 of the directive. Certain criteria remain to be defined by the Commission. Certain specified wastes cease to be regarded as waste when they have undergone a recovery, recycling and operation. Article 3.17 of the directive has defined recovery process as

*Any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfill a particular function, or waste being prepared to fulfill that function, in the plant or in the wider economy*

Substance or object having end-of-waste status should comply with specific criteria to be developed in accordance with following conditions:

- Substance or object commonly used for specific purposes
- Market and the demand for such substance or object exists
- Substance or object meets the technical requirement of the intended application or purposes and fulfills the existing legislation and standards applicable to products
- Further use substance or the object will not lead to adverse environmental and health impacts.

The criteria shall include limit values for pollutants where necessary and shall take into account of any further adverse environmental and health effects of substance or object. Therefore, it has to be noted that CCPs for trace elements extraction are not subject to waste directive. However, CCPs are subject to EU REACH Regulation.

### 5.3.2. REACH REGULATION

**REACH** -Registration, Evaluation and Authorization of Chemicals is a regulation proposed by European commission, entered into force on 1<sup>st</sup> June 2007 in order to develop chemicals registration system. This regulation replaced about 40 pieces of European Directives and Regulations [132].

REGISTRATION	EVALUATION	AUTHORIZATION	RESTRICTION
<ul style="list-style-type: none"> <li>• All substances manufactured/ imported above 1 metric ton per year are required to register</li> </ul>	<ul style="list-style-type: none"> <li>• Member states are required to evaluate the submitted dossiers fo substances for registration at ECHA</li> </ul>	<ul style="list-style-type: none"> <li>• Eliminates some substances from its uses depending on their hazardous properties to human, environment and depending on the available alternatives (ANNEX XIV)</li> </ul>	<ul style="list-style-type: none"> <li>• Regulation of manufacturing/ importing or marketing of certain substances on the market if they pose an unacceptable risk to health or to the environment (Annex XVII)</li> </ul>

The chemicals registration system, aims to improve protection of human health and environment from chemical hazards and to enhance the European Chemical industry competitiveness. Additionally, the aims of REACH regulation implementation within EU are [132]:

- To substitute the most dangerous chemicals if suitable alternatives are identified
- To reduce to a minimum research on vertebrate animals
- To promote alternative methods to conduct assessments of hazardous properties of substances
- To ensure free movement of chemicals

According to the REACH regulation, any enterprise that is manufacturing or importing the chemical substance of more than 1 metric ton per year is required to register importing/manufacturing chemicals at the central chemicals registration database, which EU Chemical Agency (ECHA) located in Helsinki, Finland operates the database. For the registration, the enterprises are required to prepare and submit a very comprehensive dossier for their manufacturing/importing chemicals according to the article 10. Quantity of the information to be submitted as chemical dossier depends on the volume of the substance to be manufactured/imported, meaning bigger volumes of production/importation per year require bigger quantities of information. Information required for general registration purpose according to Article 10 and 12 includes [133].

1. Information on the substance's characteristics:
  - a. Chemical and Physical properties
  - b. Hazard to humans and Environment
2. The identity of the manufacturer(s) or importer(s)
3. A registration required by Article 6 or by Article 7(1) or (5) shall include:
  - a. A technical dossier:
    - i. The identity of the manufacturer(s) or importer(s) as indicated in section 1 of Annex VI
    - ii. The Identity of the substance as indicated in section 2 of Annex VI (Information requirements referred to in article 10)
4. Information on the manufacture (not for imported substances) and uses of the substance
5. Classification and labeling of the substance
6. Guidance on safe use of the substance
7. Study summaries of the information derived from the application of Annexes VII (Standard information requirements for substances manufactured or imported in quantities of one tone or more) to XI (General rules for adaptation of the standards testing regime set out in annexes VII to X)
8. Robust study summaries of the information derived from the application of Annexes VII to XI or under Annex I if required
9. Proposals for testing where listed in Annexes IX (General rules for adaptation of the standard testing regime set out in annexes VII to X) and X (Standard information requirements for substances manufactured or imported in quantities of 1000 tone or more)
10. For volume of 1 to 10 tone bandage, exposure information as indicated in section 6 of Annex VI
11. A chemical safety report, if required under Article 14 (> 10 tone/year)

12. Eco-toxicological and toxicological test. The analysis of the test shall be carried out in compliance with the principles of good laboratory practice (GLP) provided for in Directive 2004/10/EC or other international standards recognized as being equivalent by the Commission or the Agency and with the provisions of Directive 86/609/EEC if applicable.

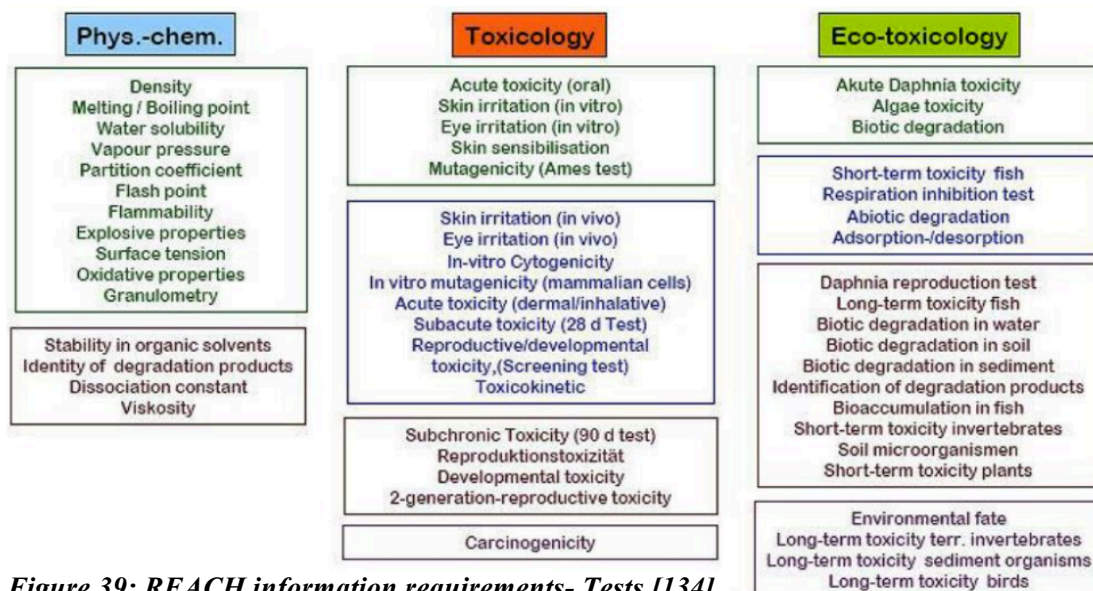
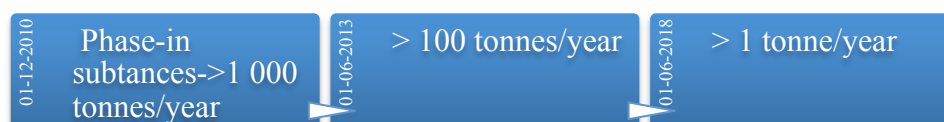


Figure 39: REACH information requirements- Tests [134]

Moreover, it is required to provide risk assessments and control measure documents for the downstream users and these information should be in the chemical's safety report and the Safety data sheets. Under the EU REACH regulation, the duty of performing, managing of risk assessment to demonstrate safe use of the introducing chemicals is transferred from Member states to the producing industries. Therefore, chemical industries are obliged to ensure that use of their chemicals is safe or possible hazard rising from their chemicals to human health and environment are adequately prevented or controlled. This is achieved through increased knowledge about the substances manufactured/imported/used/marketed in the European market.

Therefore, CCPs is a coal combustion product and are subject to REACH regulation in the case of utilizing them for trace elements extraction. As of May 2016, no enterprises have submitted dossiers for CCPs for trace element extraction purpose.

However, ECHA central chemical database has number of entries for CCPs for other numerous purposes. Pre-SIEF (Substance Information Exchange Forum) was formed amongst the coal ash producer/importer with the same EC number. The formed parties agreed about the sameness of the CCPs, defined substance Identity Profiles (SIP) in order to form Substance Information Exchange form (SIEF). This allowed them to jointly prepare and develop a registration dossier for CCPs for the defined downstream uses. The determined lead registrant within the pre-registration parties is only required to submit one registration dossier file. According to the REACH regulation, it is normally required that registration of the substance must be done before it is manufactured/imported or put on the market. However, depending on whether the substance is a phase in or a non-phase in one or on tonnage band and on hazard, there are several registration deadlines. CCPs under REACH are phase-in substance and this allows the manufacturer/importer to pre-register the CCPs, which then allows the registration in different phases over time [135].



**Table 45: Registration of CCPs (Status 30.07.2016) [135]**

EC number	EC name	Pre-registrants	Coal-combustion-products	Pre-SIEF facilitator	Consortia
231-900-3	Calcium sulfate	1619	FGD gypsum	EUROGYPSUM	Calcium Sulfate Consortium
268-627-4	Ashes (residues)	1084	FA, BA, BS FBC-ash others	STEAK GmbH (Via Knoell Consult and VHB PowerTech)	-Ash-Reach- Consortium -By-product Consortium -ASVER Consortium
300-212-6	Ashes (Residues) Cenospheres	113	CE	B-Lands Consult (inactive)/	Interest Group formed
270-708-4	Slags, coal	524	FA, BA, BS, FBC-ash, others	STEAK (via Knoel Consult and VGB PowerTech)	-Ash-REACH Consortium -By-product Consortium -ASVEP Consortium
302-652-4	SDA product >10% ash < 10% ash	99 11	SDA- products	B-Lands Consult (inactive)// UPS/UTEX active	By-Products Consortium

Consequently, the existing entries at ECHA data base regarding CCPs are for the purpose for building material industry, civil engineering, road construction, construction work in underground coal mining, recultivation and restoration purposes in open cast mines. In addition, use of CCPs in cement production is also regulated through following directives in addition of the REACH [135]:

1. EN 450- Fly ash concrete
2. prEn 13282 Hydraulic road binder
3. EN 14227 Hydraulically bounded mixtures
4. EN 206 Concrete
5. EN 120555 Lightweight aggregates
6. EN 13242 Aggregates for asphalt
7. EN 12620 Aggregates for Concrete

#### 5.4. SUMMARY

Through literature research, it was found that in 2010, more than 145 million tonnes of CCPs were produced in EU-28 member states, of which 48 million from EU-15 member states. Utilization rate of CCPs for various purposes varied across the globe, for which the available data corresponding to the year 2010 showed EU-15 member states had an utilization rate of 91%, which is the second highest in the world after Japan (96%). 52% of the utilized CCPs were in construction industry and underground mining, 40% in restoration and open cast mines, quarries and pits.



The CCPs production trend between 1993-2012 has shown that the production rate in EU-15 decreased due to number of political decisions (Kyoto protocol-2005, Climate and Energy package (EU-20-20-20)-2008) to reduce CO<sub>2</sub> and facilitation of energy from renewable sources since 2008. However, it has indicated that the total CCPs production in EU-28 did not decline as more coal is consumed in the other EU-13 member states for electricity and heat generation purposes.

It was found that the trace elements in raw coal are affected by a number of geological factors and by the forming periods. The minerals (inorganic) found in coal are associated with type of trace elements found and their occurrence of modes hence amounts in coal. There are about 120 minerals identified in coal, in which 33 of them occur in most world coal and of which 8 are abundantly found in most coal. They are quartz, clay minerals (Kaolinite, Illite, Montmorillonite, Chlorite), Pyrite, Calcite, Siderite. For this literature research, the trace element averages of the world coal were used as the reference and these values were compared with average of China and South Africa. It was observed that the world average for trace elements had varied from the Chinese and South-African average. This is due to the fact that coals sourcing from considered countries have different minerals of varying proportions, hence different amounts of trace elements. As of today, there are not many commercially operating plants or projects under development, except Alumina extraction from ash in China. Trace elements extraction processes from CCPs are very complicated and expensive process.

The partitioning behavior of trace elements found in raw coal in thermal process, in particular in fixed-bed coal gasifier were reviewed. The result showed that the volatile trace elements (Hg, As, Se, Cd, Pb) would leave the gasifier as gas phase and be separated when syngas from the gasifier goes through a particulate matter removal system, hence partitioning them into the fly ash. For the capture of these volatile trace elements in the fly ash, it is crucial to have efficient and suitable particulate matter control system upstream of the gasifier. On the other hand, the semi and non-volatile trace elements (Cr, Cu, Mn, Ni, Sn, Ti, V, Zn) would partition into the gasifier bottom ash, hence available for recovery process. Studies have found that the degree speciation of trace elements in gasification ash is less than that in the combustion ashes. This indicates that the trace elements recovery from gasification ash is less complex, cost effective and environmentally friendly option than recovering them from combustion ash. Trace elements extractions from coal combustion residues are chemically intense process, which requires use of leaching acids (requires large volumes of fresh water), caustic precipitates and organic solvents. These chemicals should be strictly maintained during extraction process to avoid unintended environmental releases or exposure to the facility operators. This would mean more chemicals are utilized in recovery from combustion ash as the speciation degree of trace elements are more in combustion than gasification process. In 2014, EU-28 member states combusted a total of 285 million tonnes of hard coal for energy generation.

Then European regulations (Waste directive, REACH) were reviewed to determine whether marketing of CCPs for trace elements recovery process would be subject to any of them. Accordingly to the EU Waste directive, CCPs for trace elements recovery takes label of “End-of-Waste-product”, hence not subject to waste directive, but is subject to the REACH regulation.

There are several CCPs registration entries on ECHA database, but none are relating to trace elements recovery process. Therefore, presently no enterprises or industries have taken the initiative to recover trace elements available in the CCPs produced in EU-28. This is mostly likely due to the fact that much remains uncertain regarding trace elements occurrence, abundance, origin and compositions in raw coal and ashes. Hence it is difficult to predict how they would react when put under thermal process and challenging to forecast in what forms they could be found in the bottom and the fly ashes. Thus, developing of optimized recovery technology for trace elements is still problematic.

If CCPs from thermal processes were to be marketed for trace elements recovery, distinct registration for bottom and fly ash should be made, as trace elements content are different. Moreover, data required according to REACH regulation to prepare a dossier for CCPs requires toxicological data. It is impossible to get sufficient toxicological information regarding trace elements found in coal to fully protect the environment and the public health when their modes of occurrence, abundance, origin and compositions are not fully understood. For the same reason, development of economically, environmentally and technologically feasible trace elements recovery technology is still under development. Depending on the extraction technologies, multiple secondary waste streams are generated, such as large volumes of contaminated water from acid leaching process, extraction solvents, which needs to be treated for contaminants in order to minimize fresh water uptake for the process or from environmental point of view. Characteristics of the CCPs available for trace element extraction vary considerably depending on various factors and this makes it difficult to develop commercialized technology, hence leads to limited understanding of future waste streams from the process as they vary considerably. These unknown future waste streams will have different impacts on environment and public health, which conducting of their toxicological assessment is impossible presently. To overcome such challenge, a particular CCPs should undergo full chemical characterization in order to determine which contaminants from the process require specialized waste handling measures.

Therefore, trace element recoveries from ashes are subject to EU REACH regulation and REACH regulation is enough to protect environment and public health if all the required data are collected for registration at ECHA. However, obtaining of full toxicological data of each trace elements and their full speciation are questionable, as they are not fully understood in the original raw coal and modes of occurrence in the ashes. Each speciation of each trace element has different toxicological properties and each speciation of every trace elements are not known. Our understanding of environmental exposure and causing environmental and health risks associated with trace element recovery from CCPs are very limited and future research and development should be done to obtain required toxicological information to develop safety recommendation and to understand toxic effects, potential routes of exposure/concentrations of generated chemical contaminants from all phases of extraction process. In addition, trace elements recovery process must be optimized in order to minimize use of hazardous chemicals, such as acids and solvent extractants. As a result, information required by EU REACH regulation and informations required protecting environment and public health are obtained. Information required by EU REACH regulation could be one of the factors that are discouraging industries to look into possibilities of recovering trace elements from CCPs.

Lack of interest in trace elements recovery from Coal Combustion Products (CCPs) could be reversed if same amount of effort and focus is paid to study trace elements recovery from Coal Gasification Products (CGPs). Because recovery of trace elements from CGPs are less complex (reduced speciation degree), hence economical and environmentally friendly compared to recovering them from CCPs. However, such shift is only possible if all the coal burning power generation facilities in EU-28 are closed and coal gasification plants to supply power demand from coal are realized.

## 6. CONCLUSION

As a result of performing literature review on coal syngas cleaning technologies, plasma methods were found to have potential in coal syngas cleaning, particularly the non-thermal plasma in coal syngas tar removal. Technological feasibility of non-thermal plasma for target gasifier (small scaled ambient fixed-bed gasifier) were investigated with help of Aspen plus V.703 and found to be feasible. From the aspen simulations, the cleaned syngas from studied technology (Gasifier-Plasma) were determined to be suitable as fuel gas for heat generation and not suitable for other applications due to high nitrogen content sourcing from air gasification and requirement of the plasma unit. Market potential for fuel gas generation with ambient fixed-bed gasifier and plasma unit were identified, which more than 8000 and 2000 gasifiers/plasma are needed in China and India respectively for the purpose of supplying heat for industrial purpose.

Initial economic analysis has shown that heat generation by fuel gas produced from coal gasification is cheaper option than burning Natural gas and LPG. The further economic analysis has shown fuel gas production cost (\$/m<sup>3</sup>) via ambient fixed-bed gasifier-plasma was found to be much cheaper than current state of art case to generate fuel gas.

**Table 46: Fuel gas production cost through two options against the current actual price of Natural gas and LPG**

	Market price (\$/m <sup>3</sup> )	Current state of art (\$/m <sup>3</sup> )	Plasma employed (\$/m <sup>3</sup> )
Natural gas	0,30	0,12	0,10
LPG	1,56	0,41	0,34

The above economic competitiveness can be achieved by complying with the stated economic conditions, which includes investing as less as possible from 300 000 USD for the plasma unit, supplying electricity demand for the plasma unit from central grid and purchasing the feed coal at 50% reduced priced than coal used in current state or art case.

Furthermore, fuel gas generation and cleaning by purposing solution would offer following advantages over the current state of art case:

- ✓ Feed flexibility- Avoids using expensive and not abundantly available anthracite type coal, which sub-bituminous coal can be obtained at 50% reduced price for the plasma configuration
- ✓ Use of fresh water eliminated – Plasma configuration does not employ any source of fresh water and this is the biggest advantageous point over the current state of art case, as it is used water is in direct contact with the fuel gas to be cleaned and pollutes the water.
- ✓ Plasma unit reforms the tar to increase the fuel gas energy stream (MJ/hr) by 20%
- ✓ Economically competitive over the current state of art cases.
- ✓ Market for ambient fixed-bed gasifier and Plasma are present (China:>8000, India> 2000)
- ✓ Patent to use non-thermal pulsed corona discharge in coal fuel gas application is not owned by anyone
- ✓ Realisation will be next to the end user and no transportation of fuel gas is needed and infrastructure of long pipelines
- ✓ Can reform high amount of tar with >95% reforming efficiency

Abundantly available coal combustion ashes are potential untapped resource for trace elements that can alleviate supply shortage of transition elements. The future of technology advancement and sustainable and efficient energy generations are dependent on availability of trace elements. EU-28 had consumed 285 million tonnes of hard coal in 2014 and their residues were available for trace elements extraction. Extraction of trace elements are subject to EU REACH regulation and such

regulation is sufficient to protect environment and public health from contaminants rising from all stages of trace elements extraction processes. However, lack of commercially available extraction technology optimized for CCPs, limited understanding of trace elements modes of occurrence, origin, and toxicological data relating to all possible chemical contaminants rising from extraction process are not well understood and are not presently available. More research and development effort must be done in order to obtain these missing information and to perform full chemical characterization of the coal ash supplied to EU to optimize trace elements extraction process for that particular coal and to identify all possible waste streams. Such that, needed toxicological data according to REACH regulation is obtained. However, it is expected to take time to fully understand toxic effects, potential routes of exposure/concentrations of generated chemical contaminants and to minimize use of hazardous chemicals (acids, solvent extractants) as trace element extraction process is chemical intense process.

If all the needed toxicological information are obtained through research and development and if it were to develop a trace elements extraction technology, coal gasification ash is more attractive than the coal combustion ash from techno-economic and environmental point of view. This is because degree of trace elements speciation in gasification ash is less than that from the combustion ash. This will lead to less complex extraction process consuming fewer chemicals, less energies; hence less waste streams for further treatment for disposal. Moreover, coal gasification is a partial oxidation process, which the gasification parameters are strictly maintained, this would reduce variations in trace elements occurrence and speciation in gasification ash, which will allow easier tailoring and optimizing of the extraction process. On the other hand, combustion process is full oxidation and high degree of variations of trace elements in combustion ash will be observed and optimization of trace elements extraction process from combustion ash will be very difficult.

## REFERENCES

1. UN News (2013). World population projected to reach 9.6 billion by 2050. Retrieved from: <https://www.un.org/development/desa/en/news/population/un-report-world-population-projected-to-reach-9-6-billion-by-2050.html> . Visited on: 20-02-2016.
2. International Energy Agency ( Dec-2015). Key coal trends excerpt from Coal Information. Retrieved from: <http://www.iea.org/publications/freepublications/publication/coal-information---2015-edition---excerpt.html> . Visited on: 07-11-2015.
3. The guardian news (2014). China and US make carbon pledge. Retrieved from: <http://www.theguardian.com/environment/2014/nov/12/china-and-us-make-carbon-pledge>. Visited on: 22-02-2016
4. Government of India, Ministry of Power (2015). Power for all. Retrieved from: [http://powermin.nic.in/upload/pdf/joint\\_initiative\\_of\\_govt\\_of\\_india\\_and\\_andhrpradesh.pdf](http://powermin.nic.in/upload/pdf/joint_initiative_of_govt_of_india_and_andhrpradesh.pdf). Visited on: 25-02-2016
5. The guardian news (2015). Tesla's Powerwall to flow batteries: a guide to the energy storage revolution. Retrieved from: <http://www.theguardian.com/sustainable-business/2015/oct/27/tesla-powerwall-batteries-flow-lithium-energy-storage-revolution>. Visited on: 28-02-2016.
6. Tesla motors (2015). Battery storage. Retrieved from: <https://www.teslamotors.com/powerwall>. Visited on: 28-02-2016
7. Center for climate and Energy solutions (C2ES) (2011). Carbon capture and storage facts. Retrieved from: <http://www.c2es.org/technology/factsheet/CCS>. Visited on: 20-02-2016
8. SASKPOWER CCS (2015). Boundary dam carbon capture project. Retrieved from: <http://saskpowerccs.com/ccs-projects/boundary-dam-carbon-capture-project/>. Visited on: 20-02-2016.
9. Sadhvi, Sh. (2015). India's right: Coal makes the world go round. Retrieved from: <http://www.spiked-online.com/newsite/article/india-is-right-coal-makes-the-world-go-round/17698#.VvFipOIrLgG>. Visited on 22-03-2016
10. Alberta Energy (2015). What is coal. Retrieved from: <http://www.energy.alberta.ca/coal/645.asp>. Visited on: 28-02-2016.
11. World coal association (2016). What is coal. Retrieved from: <https://www.worldcoal.org/coal/what-coal>. Visited on: 17-01-2016.
12. Prabhansu,A.; Malay,Kr.; Karmakar,B.; Prakash Chandra,A.; Pradip, Kr.; Chatterjee,B. Journal of Environmental Chemical Engineering. 2015, 3,689-702
13. Knoef, H. (2005). Handbook biomass gasification. The Netherlands: BTG biomass technology group B.V
14. Chamco (2015). What is gasification process. Retrieved from: <http://www.chamco.net/Gasification.htm>. Visited on: 24-01-2016.
15. Gräbner,M. (2014). Industrial Coal Gasification Technologies Covering Baseline and High-Ash Coal. Germany: Wiley-VCH Verlag GmbH and Co. KGaA
16. Bine information service (Sep-2006). Power plant with coal gasification. Retrieved from: (<http://www.bine.info/en/publications/projektinfos/publikation/kraftwerke-mit-kohlenvergasung/>: Visited on: 17-01-2016.
17. McKendry, P. (2000). Energy production from biomass gasification technologies. Journal of Bioresource Technology 83, 55–63.
18. Raj, D. Parekh. (1982). "Handbook of Gasifiers and Gas Treatment Systems (Report No: DE-AC01-78ET10159). U.S.DOE
19. Osman,T.(2007). Sasol-Lurgi Fixed-Bed Dry Bottom Gasification for Fuels and Chemicals", 2<sup>nd</sup> International Freiberg Conference on IGCC and XtL Technologies, Freiberg, Germany,
20. Weiss, M.M. (2011). A New HP Version of Lurgi's FBDB "Gasifier is Bringing More Value to Clients", Gasification Technology Conference. San Francisco, California.
21. Weiss, M.M.; Stephen, S. (2012). Lurgi Advanced MK PLUS Gasifier Technology Applied for SNG Production", Gasification Technology Conference. Washington, D.C
22. Air-Liquide Global EandC Solutions. (2015). Technology Handbook:
23. Mccoy,M .(2007). Air Liquide Will Acquire Lurgi. Retrieved from: <http://cen.acs.org/articles/85/i17/Air-Liquide-Acquire-Lurgi.html>. Visited on: 07-01-2016
24. CMU Adv. Power Plant Design Coal and biomass gasification lecture
25. National Energy technology Laboratory .(2015). Fixed(Moving) bed Gasifiers. Retrieved from: <http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/fmb>
26. Weiss, M.M.; Osman,T. (2009)Lurgi Clean Coal Technology Co –LCCT, A New Name, But A Well Proven Technology Back to Lurgi", Gasification Technology Conference, Colorado Springs, Colorado
27. National Energy Technology Laboratory (2015). Lurgi Dry-Ash Gasifier. Retrieved from: <http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/lurgi>. Visited on: 22-01-2016
28. Boerrigter, H.; Calis, H.P.; Slort, D.J.; Bodenstaff, H.; Kaandorp, A.J.; Uil, H. den; Rabou, L.P.L.M. (2004). Gas cleaning for integrated Biomass Gasification (BG) and Fischer-Tropsch (FT) systems (Report No: C—04-056), Petten, Energy research Centre of the Netherlands (ECN),



29. Boerrigter, H.; Uil, H.D.; Calis, H.P.(2003). Green diesel from biomass via Fischer-Tropsch synthesis: new insights in gas cleaning and process design, in: Pyrolysis and Gasification of Biomass and Waste, Bridgewater. United Kingdom, CPL press.
30. Ullmann's Encyclopaedia of Industrial Chemistry, 2002.
31. Waste to Energy systems (2015). Syngas: A versatile and renewable fuel. Retrieved from: <http://wastetoenergysystems.com/category/gasification/>. Visited on 18-12-2015.
32. Milne,T.A.; Evans,R.J.(1998). Biomass Gasifier Tars: Their Nature, Formation, and Conversions. Colorado, National Renewable Energy Laboratory,
33. Hasler,P.; Nussbaumer, TH.; Biomass and Bioenergy. 1999, 16, 385-395
34. Knoef, H.A.M.(2000). A review of fixed bed gasification systems for biomass. School of energy studies for agriculture, India
35. Hoffmann, A.; Stein, L.; Bradshaw, P. Applied Mechanics review. 2003, 56, 28-29
36. Seville, J.P.K. (1997). Gas Cleaning in Demanding Applications. New York: Blackie Academic and Professional, London
37. McDonald, J.R.; Dean, A.H. (1982). Electrostatic Precipitator Manual. New Jersey: Noyes Data Corp.
38. Schiffner, K.C.; Hesketh H.E.. (1996) Wet Scrubbers. Lancaster, PA: Technomic
39. Hasler, P.; Buehler,R; Nussbaumer,TH. (1998). Biomass for energy and industry, 10th European Conference and Technology Exhibition, Wurzburg, Germany
40. Lovell, R.; Dylewski,S.; Peterson,C. (1981). Control of Sulfur Emissions from Oil Shale Retorts, EPA, Cincinnati, Ohio
41. Vamvuka,D.; Arvanitidis,C.; Zachariadis,D.; Environ. Eng. Sci. 2004, 21;4
42. Dou,B.; Wang,C.; Chen,H.; Song,Y.; Xie,B.; Xu,Y.; Tan,C. Chemical Engineering Research and Design. 2012. 90, 1901-1917
43. Korens,N.; Simbeck, D.R.; Wilhelm, D.J. Process Screening Analysis of Alternative Gas Treating Sulfur Removal for Gasification, SFA Pacific, Mountain View, California, 2002.
44. Steynberg, M. D. (2004). Fischer–Tropsch Technology, Amsterdam: Elsevier.
45. Maniatisa, K., Beenackers ,A.A.C.M. (2000). Tar Protocols. IEA Bioenergy Gasification Task. Journal of Biomass and Bioenergy 18, 1-4.
46. Energy Research centre of The Netherlands (2015). Biomass technology and knowledge exchange. Retrieved from: <https://www.ecn.nl/energy-research/biomass/>. Visited on: 14-11-2015
47. Energy Research centre of The Netherlands. (X). Thesites: Website for tar dew point calculation (Report No: ECN-C—02-090). Petten, Energy Research centre of The Netherlands
48. Zwart , R. W. R.; (2009). Gas Cleaning Downstream Biomass Gasification – Status Report, Petten, Energy and Research Centre of The Netherlands,
49. Vreugdenhil, B. J.; Zwart, R.W.R. (2009). Tar Formation in Pyrolysis and Gasification, Biomass, Coal and Environmental Research, Petten, Energy and Research Centre of The Netherlands.
50. Jess, A. Fuel. 1996. 75, 1441-1448
51. Nair.S.A.; Yan,K.; Pemen,A.J.M.; Winands, F.M.G.; Van Leuken, H.E.M.; Van Heesch, G.J.J.; Ptasinski, K.J.; Drinkenbrug, A.A.H. Journal of Electrostatics. 2004, 61, 117-127
52. Bruinsma, O. S. L.; Geertsma, R. S.; Bank, P.; Moulijn, J. A. Fuel. 1988, 67, 327-333
53. Bosmans,A.; Wasan, Shivanand,W.; Helsen,L. (2013). WASTE TO CLEAN SYNGAS:AVOIDING TAR PROBLEMS. Department of Mechanical Engineering, KU Leuven, Heverlee, Belgium
54. Vreugdenhil, B. J.; Zwart, R. W. R. (2009). Tar Formation in Pyrolysis and Gasification (Report No.08-087). Petten, Energy and Research centre of the Netherlands.
55. Woolcock, P.J.; Brown, R.C. Biomass and Bioenergy. 2013, 52, 54-84.
56. Milne, T. A.; Evans, R. J.; Abatzoglou,N.(1998). Biomass Gasifier “Tars”: Their Nature, Formation, and Conversion. Colorado, National Renewable energy laboratory.
57. Sutton,D.; Kelleher, B.; Ross, J. R. H. Fuel Processing Technology. 2001, 73, 155-173
58. Tregrossi, A.; Russo, C.; Stanyione, F.; Barbella, R.; Ciajolo, A. (1999). The combustion of benzene in rich premixed flames at atmospheric pressure. Napoli, Dipartimento di Ingegneria Chimica, Universita.
59. Fjellerup, J.; Ahrenfeldt, J., Henriksen, U., Gobel, B.(2005). Formation, decomposition, and cracking of biomass tars in gasification ( Report No:MEK-ET-2005-05). Technical Universityof Denmark.
60. Yung, M.M.; Jablonski, W.S.; Magrini-Bair, K.A. Energy fuels. 2009, 23, 1874-1887.
61. Chan, F.L.; Tanksale, A. Sustainable Energy Review of recent developments in Ni-based catalysts for biomass gasification, Renew and Sustainable Energy Reviews. 2014, 38, 428-438
62. Dayton, D. (2002). A Review of the Literature on Catalytic Biomass Tar Destruction (Report No: NREL/TP-510-32815). Colorado, National Renewable Energy Laboratory
63. Anis,S.; Zainal, Z.A. Reneable and Sustainable Energy Reviews. 2011, 15, 2355-2377
64. Sutton, D.; Kelleher,B.; Ross, J.R.H. Fuel Processing technology. 2001, 73, 155-173
65. Simell, P.A.; Leppalahti, J.K.; Bredenberg, J.B.; Fuel process technology. 1992, 71, 211-218
66. Hu, G.; Xu, S.; Li, S.; Xiao, C.; Liu, S. Fuel Process Technology. 2006, 87, 375-382
67. Devi,L.; Craje,M.; Thune,P.; Ptasinski,K.J.; Janssen, F.J.J.G. Applied Catalysis A. 205, 294, 68-69
68. Corma, A. Journal of catalysis. 2003, 216, 298-312

69. Torres, W.; Pansare, S.S.; Goodwin, J.G. Hot gas removal of tars, ammonia, and hydrogen sulfide from biomass gasification gas. *Catalysis reviews*. 2007, 49, 407-456
70. Dou, B.; Gao, J.; Sha, X.; Baek, S.W. *Applied Thermal Engineering*. 2003, 23, 2229-2239
71. Buchireddy, P.R.; Bricka, R.M.; Rodriguez, J.; Holmes, W. *Energy and Fuels*. 2010, 24, 2707-2715
72. Pemen, A.J.M.; Nair, S.A.; Yan, K.; Van Heesch, E.J.M.; Ptasiniski, K.J.; Drinkenburg, A.A.H. *Plasma and Polymers*. 2003, 8, 209-224.
73. Chang, J.S. *Science and Technology of Advanced Materials*. 2001, 2, 571-576
74. Vandembroucke, A.M.; Morent, R.; Geyter, N.De.; Leys, C. *Journal of Hazardous Materials*. 2011, 195, 30-54
75. Nair, A.S. (2004). Corona plasma for tar removal (Report No: ISBN 90-386-2666-5) . Eindhoven, Technische Universiteit Eindhoven.
76. Nair, S.A.; Yan, K. (?). Corona-Induced Non-Thermal Plasma for Gas Cleaning (Report No: 1128). Eindhoven, Eindhoven University of Technology,
77. Teislev, B. (2002). Harboøre – Woodchips updraft gasifier and 1500 kW gas-engines operating at 32% power efficiency in CHP configuration. Kolding, Babcock and Wilcox Volund RandD Centre Denmark
78. Boerrigter, H.; Van Paasen, S.V.B.; Bergman, P.C.A.; Könemann, J.W.; Emmen, R.; Wijnands, A. (2005). Tar removal technology Proof –of-Concept for application in integrated biomass gasification combined heat and power systems (Report No: ECN-C-05-009). Petten, Energy Research centre of The Netherlands.
79. Zwart, R.; Van der Heijden, S.; Emmen, R.; Dall Bentzen, J.; Ahrenfeldt, J.; Stoholm, P.; Krogh, J. (2010). Tar removal from low-temperature gasifiers (Report No: ECN-E--10-008). Petten, Energy research centre of the Netherlands.
80. Balas, M.; Lisy, M.; Skala, Z.; Pospisil, J. (2014). Wet scrubber for cleaning of syngas from biomass gasification, *Advances in Environmental Sciences, Development and Chemistry*
81. Changsha Kaiyuan Instruments Co., Ltd. (2014). Coal knowledge, Basis of coal. Retrieved from: <http://www.ckic.net/FocusShow.asp?id=837&andcid=616>. Visited on: 12-10-2015.
82. Alibaba global trade (01-Dec-2015). Small scaled FBDB gasifiers. Retrieved from. [http://www.alibaba.com/product-detail/clean-coal-gasification-plant-china\\_1769207245.html?spm=a2700.7724838.35.1.NJBSg0ands=p](http://www.alibaba.com/product-detail/clean-coal-gasification-plant-china_1769207245.html?spm=a2700.7724838.35.1.NJBSg0ands=p). Visited on: 01-12-2015.
83. Van Dyk, J.C.; Keyser, M.J.; Coertzen, M. (2004). SASOL's Unique Position in Syngas Production from South African Coal Sources using SASOL-Lurgi Fixed Bed Dry Bottom Gasifiers. 21<sup>st</sup> Annual International Pittsburgh Coal conference, Osaka, Japan.
84. Air-Liquide. (2015). Coal and Coke analyzing date, Frankfurt, Germany
85. Clarke-Energy. (2015). Gas Engine Energy balance. Retrieved from: <https://www.clarke-energy.com/gas-engines/>. Visited on: 25-11-2015.
86. The University of York. (2014). The Essential Chemical Industry online: Ammonia production. Retrieved from: <http://www.essentialchemicalindustry.org/chemicals/ammonia.html>
87. Yang, C.J.; Zhou, Y.; Jackson, R.B. *Utilities Policy*. 2014, 28, 12-21
88. Xie, H.; Yu, Zhuang.; Wu, Jing. *Procedia Engineering*. 2011, 21, 1145-1151
89. Haibo, W. (2014). Status and Prospects of China's Natural Gas Market. The 8<sup>th</sup> IEEJ/CNPC Research meeting, Tokyo, Japan
90. China Coal Resource. (2015). Coal price by port, type, province and Export Country. Retrieved from: <http://en.sxcoal.com/74/0/datalist.html> : Visited on 01-12-2015.
91. International Energy Agency. (2013). China, People's Republic of: Electricity and Heat for 2013. Retrieved from: <http://www.iea.org/statistics/statisticsearch/report/?country=China&product=electricityandheat>: Visited on: 20-12-2015.
92. Statista. (2016). India: Total population from 2010 to 2020 (in millions). Retrieved from <http://www.statista.com/statistics/263766/total-population-of-india/>. Visited on: 20-12-2015.
93. International Energy Agency Statistics. (2015). Key Natural Gas Trends excerpt from: Natural Gas information. Paris.
94. Van Paasen, S.V.B.; Rabou, L.P.L.M.; Bär, R. (2004). Tar removal with a wet electrostatic precipitator (ESP); Parametric study. Petten, Energy Research Centre of The Netherlands <https://www.ecn.nl/docs/library/report/2004/rx04038.pdf>. Visited on: 7-11-2015.
95. Beijing International (2016). Guide to heating, Electricity, Water and Gas Policies and Procedures. Retrieved from: [http://www.ebeijing.gov.cn/feature\\_2/GuideToHeatingElectricityWaterAndGas/Electricity/t1107517.htm](http://www.ebeijing.gov.cn/feature_2/GuideToHeatingElectricityWaterAndGas/Electricity/t1107517.htm). Visited on 05-01-2016
96. Robert H. Perry.; Don W. Green (1997). Perry's Chemical Engineers' handbook: McGraw-Hill Professional
97. Kilpnen, P.; Zevenhoven, R (2001). Control of pollutants in flue gas and fuel gases. Finland: Helsinki University of Technology/Mechanical Engineering
98. Heidrich, C.; Feuerborn, H.J.; Weir, A.; (2013). Coal combustion products: A Global Perspective, Essen, European coal combustion products Association
99. Feuerborn, H.J. (2014). Forecast in power production and impacts of CCPs in Europe. Conference "Ashes from TPPs-removal, transport, processing, landfilling, Moscow, Russia-M.: Printing Centre, 2-14.-pp.125-132
100. European Coal Combustion Association. (2010). Statistics on Production and Utilization of CCPs in Europe (EU-15). Retrieved from: <http://www.ecoba.com/ecobaccpprod.html>. Visited on: 05-04-2016



101. Kyoto protocol on the United Nations Framework Convention on Climate change
102. Feuerborn, H.J. (2014). Forecast in power generation and impact of CCPs in Europe. Essen, Germany, European Coal combustion products association.
103. Yao, Z.T.; Xia, M.S.; Sarker, P.K.; Chen, T. Fuel. 2014, 120, 74-85
104. Lucid Insight Ltd (2014). Global Review- Commercial Recovery of Metals from Coal Ash. Retrieved from: [www.lucid-insight.com/briefings](http://www.lucid-insight.com/briefings). Visited on: 10-04-2016
105. Nalbandian, H. (2012). Trace element emission from coal. IEA Clean Coal centre
106. Woolley, D.R.; Morss, E.M. (2000). The clean air act amendments of 1990: Opportunities for promoting renewable energy (Final report prepared by NREL for US DOE.DE-AC36-99-GO10337. Washington, D.C: United States.
107. Schweinfurth, S.P.; Finkelman, R.B. (2003). Coal-A Complex natural resource. An overview of factors affecting coal quality and use in the United States. US Department of the Interior, U.S. Geological Survey, 1143.
108. Raask, E. Energy combustion science. 1985, 11, 97-118
109. Speight, J.G. (2005). Handbook of Coal Analysis. New Jersey: John Wiley and Sons, Inc (pp 222)
110. Finkelman, R. B. Fuel processing Technology. 1994. 39, 21-34
111. Finkelman, R.B. (1995). Modes of occurrence of environmentally sensitive trace elements in coal. Dordrecht, The Netherlands. Kluwer Academic Publisher.
112. Finkelman, R.B.; Brown, R.D. (1991). Coal as a host and as an indicator of mineral resources. Peters, DC.
113. Dai, S.F.; Ren, D.Y.; Chou, C.L.; Finkelman, R.B.; Seredin, V.V.; Zhou, Y.P. International Journal Coal Geology. 2012. 94, 3-21
114. Wagner, N.J.; Hlatschwavo, B. International Journal of Coal Geology. 2005. 63, 228-246
115. Ketris, M.P.; Yudovich, Ya.E. International Journal Coal Geology. 2009. 78, 135-148
116. Kema (1997). Behavior, control and emissions of trace species by coal-fired power plants in Europe- Report 83428.SP.08 97P01. Arnhem, The Netherlands
117. Brown, J.R. Fuel process technology. 1994. 39, 139-157
118. Erickson, T.A.; Galbreath, K.C.; Zygarlicke, C.J., Hetland, M.D.; Benson, S.A (1999). Trace element emissions project. Final Technical progress report for U.S. Department of Energy Contract, Energy and Environmental Research Center
119. Helbe, J. Fuel. 1986. 75, 931-939
120. Reed, G. Science. 1994. 20, 115-138
121. Shuquin, L.; Yongtao, W.; Oakley, J. Fuel process. 2006. 87, 209-215
122. Brown, J.R (1992). Toxic material emitted from coal-fired technologies; Assessment of sources, in site generation control options, measurement and environmental effects. Pittsburgh. Report prepared by SAIC
123. Bunt, J.R.; Waanders, F.B. Fuel. 2008. 87, 2374-2387
124. Bale, C. W.; Chartrand, P.; Degterov, S.A.; Eriksson, G.; Hack, K.; Manfoud, R (2002). Factstage thermodynamical software and databases, Herzogenrath, Germany. GTT-technologies)
125. Bunt, J.R.; Waanders, F.B. Fuel. 2009. 88, 961-969
126. Hlatschwayo, T.B.; Wagner, N.J. (2005). The partitioning behaviour of trace elements during gasification. Proceedings of the ICCandT conference. Okinawa, Japan.
127. Hui, Z., Xiaoyi, Z. Chemical Speciation and Bioavailability. 2009. 21, 93-97
128. Eurostat. (2015). Coal consumption statistics. Retrived from: [http://ec.europa.eu/eurostat/statistics-explained/index.php/Coal\\_consumption\\_statistics](http://ec.europa.eu/eurostat/statistics-explained/index.php/Coal_consumption_statistics). Visited on: 15-05-2016
129. Rogankov, M.P. (2014). Ash and Slag handling analytics on the experience of resolving the coal ash handling problem in different countries world wide. Moscow, Ecolopolis ltd.
130. Peter, Q.(2013). Waste Hierarchy. Retrieved from: <http://www.wtert.eu/default.asp?Menu=14&ShowDok=25>. Visited on: 20-05-2016
131. EEC. (2008). DIRECTIVE 2008/98/EC of the European parliament and of the council of 19 November 2008 on waste and repealing certain directives. Retrieved from: <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32008L0098>. Visited on 20-05-2016
132. EEC. (2006). REGULATION (EC) No 1907/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL, concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Retrieved from: [http://eur-lex.europa.eu/legal\\_content/EN/TXT/PDF/?uri=CELEX:32006R1907&from=en](http://eur-lex.europa.eu/legal_content/EN/TXT/PDF/?uri=CELEX:32006R1907&from=en). Visited on: 24-04-2016
133. European Chemical Agency (2016). Understanding REACH regulation. Retrieved from: <http://echa.europa.eu/regulations/reach/understanding-reach>. Visited on: 27-04-2016
134. Andrzej, J.; Przemyslaw, O. (2014). REACH as basis for safe coal combustion products management. State regulation measure to encourage increase in coal ash utilization in in Poland and European trends in coal ash utilization. Warsaw, Poland
135. European Coal Combustion Products Association e.V (2013). Coal combustion Products and REACH (Status 30-07-2012). Retrieved from: [http://www.ecoba.com/reach\\_ccps.html](http://www.ecoba.com/reach_ccps.html). Visited on: 26-04-2016

## APPENDICES

### A:CASE STUDIES

As last part of the thesis, number of case studies were conducted and summary of these case studies are summarized and represented in the appendices section:

**CASE STUDY 1:** Compatibility of pulsed corona discharge plasma with biomass gasifier ‘Hylowatt’ studied. Air Liquide and CMI took a stake in the capital of Xylowatt on 5<sup>th</sup> February, 2014. Xylowatt is a company active in clean gas solution from biomass and waste materials.

**CASE STUDY 2:** Nickel-based catalyst offered by Danish catalysis company Haldor- Topsoe is one of the most promising alternative to pulsed corona discharge plasma for tar removing or reforming. Therefore, comparison of Haldor-Topsoe’s nickel-based tar reforming catalyst against pulsed corona discharge plasma is conducted.

**CASE STUDY 3A:** The maximum temperature that reaches within the gasification process is crucial, as it has to correlated to ash fusion temperature of the feed coal. Therefore, the maximum temperature that it reaches is calculated with help of Aspen simulation result and combustion products. Then, sensitivity analysis on maximum temperature as a function of steam/oxygen is carried out.

**CASE STUDY 3B:** Temperature of the syngas exiting the ambient fixed-bed gasifier is determined based on heat balance of the system. For the heat balance, heat effect from the coal moisture taken into account.

### B: PROPOSALS FROM CHINESE COMPANIES OBTAINED THROUGH ALIBABA(<http://www.alibaba.com>)

**B1:**Proposals for fuel gas generation, consisting of gasifier and fuel gas cleaning equipments.

**B2:** Proposals for gas-engine