ΕΘΝΙΚΟ ΜΕΤΣΟΒΙΟ
ΠΟΛΥΤΕΧΝΕΙΟ
ΣΧΟΛΗ ΜΗΧΑΝΟΛΟΓΩΝ ΜΗΧΑΝΙΚΩΝ
ΤΟΜΕΑΣ ΘΕΡΜΟΤΗΤΑΣ
ΚΑΘΗΓΗΤΗΣ ΔΡ. ΕΜΜ. ΚΑΚΑΡΑΣ

Energie Systeme
Lehrstuhl für Energiesysteme
TUM

ΔΙΠΛΩΜΑΤΙΚΗ ΕΡΓΑΣΙΑ:

« Αριθμητική Προσομοίωση Αεριοποίησης Άνθρακα σε Συνθήκες Υψηλής Θερμοκρασίας και Πίεσης »

Του φοιτητή

Λύρα Θεόδωρου

Επιβλέποντες Καθηγητές:
Καθηγητής Δρ. Κακαράς Εμμανουήλ, Ε.Μ.Π.
Prof. Dr. –Ing. Hartmut Spliethoff, TUM

Επιβλέποντες Συνεργάτες:
Δρ. Σωτήριος Καρέλλας
Διπλ. Μηχ. Θεόδωρος Παπαδόπουλος

ΠΕΡΙΛΗΨΗ ΔΙΠΛΩΜΑΤΙΚΗΣ ΕΡΓΑΣΙΑΣ:

Η ανθρωπότητα έχει φθάσει σε κομβικό σημείο. Η ανθρώπινη κατανάλωση είναι τώρα 23% μεγαλύτερη από την ικανότητα της φύσης να αναπαραχθεί ή να απορροφησεί το «οικολογικό ίχνος» μας. Τα επίπεδα διοξειδίου του άνθρακα είναι μεγαλύτερα από οποιαδήποτε στιγμή τα τελευταία 650.000 χρόνια η θερμοκρασία επιφάνειας της γης είναι θερμότερη κατά τη διάρκεια αρκετών προηγούμενων δεκαετιών απ'ό, τι κατά τη διάρκεια οποιασδήποτε συγκρίσιμης περιόδου εδώ και τουλάχιστον 400 χρόνια. Η αλλαγή του κλίματος που επιφέρει η παγκόσμια αύξησης της θερμοκρασίας λόγω του φαινομένου του θερμοκηπίου είναι ένα γεγονός. Επίσης γεγονός είναι το ότι η εποχή της προσανατολισμένης στο φτηνό πετρέλαιο οικονομίας έχει περάσει ανεπιστρεπτεπτεί. Ο πλανήτης δοκιμάζεται από την ραγδαία αύξηση της ζήτησης πετρελαίου, τη μειωμένη προσφορά και τις υψηλές τιμές. Αυτή η ύπαρξη χάσματος μεταξύ της προσφοράς και της ζήτησης δεν είναι ένα μελλοντικό σενάριο, αλλά συμβαίνει ήδη και αυξάνεται από το 2005. Το χάσμα είναι ακόμα σχετικά μικρό, αλλά θα διευρυνεται έτος με το έτος και θα προκαλέσει περεταίρω ανόδους των τιμών και πιθανά προβλήματα ανεφοδιασμού.

Τα προαναφερθέντα περιβαλλοντικά προβλήματα και η έλλειψη πετρελαίου δημιουργούν την επιτακτική ανάγκη, να απελευθερωθεί η παγκόσμια οικονομία από την εξάρτηση της από το πετρέλαίο και να κινηθεί προς καθαρές μορφές ενέργειας. Ο άνθρακας χρησιμοποιείται ήδη ευρέως στην ενεργειακή παραγωγή και είναι το αφθονότερο στερεό καύσιμο στον κόσμο. Σε ισοδύναμη ποσότητα πετρελαίου, υπάρχει περίπου δύο φορές περισσότερος ανακτήσιμος άνθρακας απ' ό, τι πετρέλαιο και φυσικό αέριο μαζί. Συνεπώς, ο άνθρακας είναι και θα συνεχίσει να είναι ενας σημαντικός ενεργειακός πόρος. Με 41% της παγκόσμιας παραγωγής ηλεκτρικής ενέργειας να προέρχεται από την χρήση του άνθρακα ως καύσιμο, είναι σαφές ότι δεν μπορεί να υπάρξει απόλυτη ενεργειακή ανεξαρτησία από τα στερεά καύσιμα. Κατά συνέπεια, η περιβαλλοντικά πιό φιλική χρήση των ορυκτών καυσίμων και συγκεκριμένα του άνθρακα, είναι η πρόκληση του μέλλοντος.

Σύμφωνα με τη Διακυβερνυτική Επιτροπή για την Αλλαγή Κλίματος (Intergovernmental Panel on Climate Change – IPCC) και το Διεθνές Πρακτορείο Ενέργειας (International Energy Agency – IEA), οι τεχνολογίες δέσμευσης και απομάκρυνσης άνθρακα (Carbon Capture and Sequestration – CCS) έχουν τη δυνατότητα μείωσης των συνολικών εκπομπών αερίων του θερμοκηπίου από 20 έως 30% μέχρι το 2050. Η Δέσμευση και Απομάκρυνση Άνθρακα (CCS) είναι ένας ευρύς όρος που καλύπτει διάφορες τεχνολογίες που μπορούν να χρησιμοποιηθούν για να συλλάβουν το διοξείδιο του άνθρακα από σημειακές πηγές, όπως οι εγκαταστάσεις παραγωγής ενέργειας και άλλες βιομηχανικές εγκαταστάσεις, να το συμπιέσουν, και να το μεταφέρουν κυρίως μέσω σωληνώσεων σε κατάλληλες θέσεις όπου θα εγχυθεί σε γεωλογικούς σχηματισμούς σε μεγάλο βάθος κλατω από την επιφάνεια για την επ’ αόριστω απομόνωση του από την ατμόσφαιρα.

Τρεις κύριες προσεγγίσεις μπορούν να χρησιμοποιηθούν για την δέσμευση του CO_2 από τις εγκαταστάσεις παραγωγής ενέργειας: Η δέσμευση μετα την καύση (Post – Combustion Capture), η οποία αναφέρεται στο διαχωρισμό του CO_2 από τα καυσαέρια μιας διαδικασίας καύσης. Οι πηγές καυσίμων μπορούν να είναι οποιοσδήποτε υδρογονάνθρακας, όπως το κάρβουνο, το φυσικό αέριο, ή το πετρέλαιο. Η δέσμευση προ της καύσης (Pre – Combustion Capture) που περιλαμβάνει την παραγωγή αερίου σύνθεσης (μονοξείδιο άνθρακα και υδρογόνο – CO,H_2), ακολουθούμενη από αντίδραση μετατροπής του CO σε CO_2. Το CO_2 έπειτα διαχωρίζεται από το υδρογόνο, το οποίο μπορεί να χρησιμοποιηθεί σαν καύσιμο σε στρόβιλο ή για αλλη χρήση. Τέλος, η δέσμευση με καύση πλούσια σε οχυγόνο (Oxy – Fuel Combustion) η οπία και περιλαμβάνει την καύση του καυσίμων σε περιβάλλον πλούσιο σε οξυγόνο, ώστε να αυξηθεί υπερβολικά η συγκέντρωση του CO_2 των καυσαερίων (συνήθως >80%) και να διευκολύνθει έτσι ο διαχωρισμός του.

Η δέσμευση άνθρακα προ της καύσης συνδέεται συνήθως με την ολοκληρωμένη τεχνολογία ηλεκτροπαραγωγής συνδυασμένου κύκλου με αεριοποίηση (Integrated Gasification Combined Cycle - IGCC). Οι περισσότερες μελέτες έχουν καταλήξει, ότι είναι αποδοτικότερο οικονομικά να χρησιμοποιηθούν τεχνολογίες δέσμευσης άνθρακα προ της καύσης σε συνδιασμό με τεχνολογία IGCC επειδή το CO_2 μπορεί να δεσμευθεί σε υψηλότερες πιέσεις σε σχέση με τις άλλες τεχνολογιες δέσμευσης.

Τα συστήματα IGCC συνδυάζουν μια μονάδα αεριοποίησης άνθρακα με μια με μονάδα συμπαραγωγής ενέργειας. Το πρώτο στάδιο είναι η διαδικασία αεριοποίησης άνθρακα όπως αναφέρεται ανωτέρω. Το δεύτερο στάδιο περιλαμβάνει την καύση του καθαρού αερίου σε έναν συμβατικό αεριοστρόβιλο παράγοντας ηλεκτρική ενέργεια. Το θερμό καυσαέριο χρησιμοποιείται σε έναν ατμοπαραγωγό ανάκτησης θερμότητας (HRSG), δημιουργόντας τον ατμό που εκτονώνεται σε έναν ατμοστρόβιλο παράγοντας περεταίρω ενέργεια.

Μόνο μερικά από τα πλεονεκτήματα της τεχνολογίας IGCC είναι ο υψηλός θερμικός βαθμός απόδοσης (μέχρι 50%), τα χαμηλότερα ποσοστά εκπομπών, ο μικρός όγκος των στερεών αποβλήτων και ευελιξία στο είδος της καύσιμης ύλης. Λόγω των παραπάνω πλεονεκτημάτων, το ενδιαφέρον στον τομέα της αεριοποίησης αυξάνεται συνεχώς και έχει δημιουργήσει επίσης την ανάγκη προσέγγισης σε επίπεδο αριθμητικής προσομοίωσης. Τα οφέλη μιας τέτοιας προσέγγισης μπορούν να μεταφραστούν ως χαμηλότερο αρχικό κόστος σε ένα πιθανό εγχείρημα στον χώρο της αεριοποίησης και μιας μεγαλύτερης αποδοτικότητας κατα την συνέχεια, λόγω λειτουργίας σε βέλτιστες συνθήκες.

Εκτενείς επιστημονικές έρευνας έχουν λάβει χώρα στον τομέα της αριθμητικής μοντελοποίησης της αεριοποίησης του άνθρακα και με πολύ επιτυχή αποτελέσματα. Εντούτοις φαίνεται να υπάρχει μια έλλειψη στοιχείων προσομοίωσης για πιέσεις αεριοποίησης της τάξης των 50 bar. Το πρόγραμμα HotVeGas - HHV του πολυτεχνείο του Μονάχου (TUM) στοχεύει στην πραγματοποίηση της απαραίτητης έρευνας στον τομέα της αεριοποίησης και των

άλλων μεταβλητών από τις οποίες αποτελείται μία εγκατάσταση παραγωγής ενέργειας τεχνολογίας IGCC.

Ο σκοπός αυτής της διπλωματικής είναι να συμβάλει στο ανωτέρω έργο με την ανάπτυξη ενός αριθμητικού μοντέλου της αεριοποίησης άνθρακα σε παρασυρόμενη ροή (entrained flow gasification) σε συνθήκες υψηλής πίεσης και θερμοκρασίας με τη χρήση του εμπορικού CFD προγράμματος ANSYS CFX. Για την δημιουργία του μοντέλου, έγινε έρευνα σε όλη την σχετική με το θέμα βιβλιογραφία. Το μοντέλο που αναπτύχθηκε είναι σε θέση να προβλέψει τη σύσταση του αερίου που παράγεται από την αεριοποίηση του άνθρακα, και άλλες σημαντικές μεταβλητές όπως η θερμοκρασία και η ταχύτητα.

Τα αποτελέσματα που εξήχθησαν αναφέρονται σε συνθήκες πίεσης από 5 μέχρι 50 bar και θερμοκρασίες στο τοίχωμα του αεριοποιητή της τάξης των 1600 ° C. Οι ρυθμίσεις του μοντέλου μπορούν να τροποποιηθούν εύκολα και να προβλέψουν επιτυχώς τη συμπεριφορά της διαδικασίας αεριοποίησης σε ποικίλες αρχικές συνθήκες, το οποίο καθιστά το μοντέλο ευέλικτο και κατάλληλο για να εξετάσει διαφορετικούς συνδυασμούς αρχικών συνθηκών για τη βελτιστοποίηση ενός πραγματικού αεριοποιητή.

Συγκεκριμένα : οι προσομοιώσεις αεριοποίησης έγιναν σε πιέσεις 5, 25 και 50 bar και επικουρικά, με λόγους μαζας οξυγόνου/καυσίμου $\lambda = 0.8$, 0.9 και 1.0 . Μερικά από τα συμπεράσματα που εξήχθησαν είναι τα ακόλουθα:

- Η αύξηση της πίεσης οδηγεί σε μείωση της σύστασης σε υδρογόνο και μονοξείδιο του ανθρακα του παραγόμενου αερίου, παρ’ ολ’ αυτά η μείωση αυτή δεν είναι σημαντική.
- Όσο αυξάνεται η πίεση αυξάνεται και η μάζα του μεθανίου, του διοξειδίου του ανθρακα και του ατμού που παράγεται.
- Η παροχή οξυγόνου είναι μια πολύ σημαντική μεταβλητή της διαδικασίας της αεριοποίησης. Πλεόνασμα οξυγόνου συντελεί στην αύξηση της συγκέντρωσης H_2 και του CO στο παραγόμενο αέριο.

Οι επιδόσεις του μοντέλου κρίνονται γενικά ικανοποιητικές. Ωστόσο, η σύγκριση των αποτελεσμάτων των προσομοιώσεων με πειραματικά δεδομένα θα ήταν απαραίτητη επειδή, το μοντέλο εξετάστηκε για υψηλές πιέσεις αεριοποίησης όπου η βιβλιογραφία είναι φτωχή και δεν υπάρχει κανένα επαρκές στοιχείο σχετικά με τα χημικούς ρυθμούς αντίδρασης και τη χημεία της αεριοποίησης γενικότερα .

Η περαιτέρω ανάπτυξη του μοντέλου είναι φυσικά απαραίτητη εάν το πρότυπο στοχεύει για να χρησιμοποιηθεί ως μέσο αξιολόγησης και βελτιστοποίησης υπάρχοντα αεροποιητή αλλά σε χαμηλότερο επίπεδο χρήσης, μπορεί να παρέχει με ικανοποιητική ακρίβεια πληροφορίες για την λειτουργία ενός αεριοποιητή.

Abstract

This Diploma Thesis has as a goal to create a numerical model that will simulate the coal gasification process that will take place in the gasifier that will be built in the TUM for the HotVeGas Project. The model that was created simulates with the use of the Ansys CFX program, the gasification and pyrolysis of coal particles inside an entrained flow gasifier in conditions of high temperature (up to 1800° C) and pressure (up to 50 bar). The results of a model like that can be used to predict the products of the gasification process so that we can determine the benefits of using this technology in applications that will be in the first line of energy production from coal, in the next decade, such as the Integrated Gasification Combined Cycle.

Key Words: numerical simulation, coal gasification, pyrolysis, entrained flow gasifier, IGCC, CFX

Contents

Figures

Tables

Abbreviations

- ASTM: American Society for Testing and Materials
- CCS : Carbon Capture and Sequestration
- CFB: Circulating Fluidized Bed
- CFC: Chloro-fluoro-carbons
- Daf : Dry, ash-free
- Db : Dry basis
- Dmmf : Dry, mineral matter-free
- EIA : Energy Information Administration
- FGD: Flue Gas Desulfurization
- IEA: International Energy Agency
- IGCC : Integrated Gasification Combined Cycle
- IGT: Institute of Gas Technology
- IPCC : Intergovernmental Panel on Climate Change
- KIER: Korea Institute of Energy Research
- Maf : Moist, ash-free
- Mmmf : Moist, mineral matter-free
- PFBC : Pressurized Fluidized Bed Combustion
- PC: Pulverized Coal
- PCC : Pulverized Coal Combustion
- SCPC: Supercritical Pulverized Coal
- USCPC: Ultra-Supercritical Pulverized Coal

Symbols

- ρ : Density
- $\mathbf{U}$: Vector of velocity $\mathbf{U}(x,y,z)$
- t : Time
- p : Static Pressure
- τ : Shear Stress
- S_M : Momentum Source
- S_E : Energy Source
- μ : Molecular Dynamic Viscosity
- δ : Delta function
- h_{tot} : Specific total enthalpy
- h : Specific static enthalpy
- λ : Thermal conductivity
- λ_{af} : Air-Fuel Ratio
- K : Kinetic Energy

1 Introduction

Humanity has reached the point of no return. Human consumption is now 23% larger than nature's capacity to regenerate or to absorb our "ecological footprint." Environmental trends make it clear that either human society changes or eventually nature will change society. It is increasingly passé and ignorant to think that humanity has to choose between economic growth and environmental protection. Carbon dioxide levels are now greater than at any time in the last 650,000 years; the surface temperature of Earth has been warmer over the past several decades than during any comparable period in at least 400 years; six of the last eight years were the hottest on record. Climate change due to global warming is a fact.

What is also a fact is that the times of cheap oil driven economy are forever over. The planet is currently experiencing a time of severe growth of oil demand, declining supply, expensive exploration, higher prices, and huge regional and geopolitical tensions. To describe the situation in an one long nutshell line: more people on earth, more prosperity on earth, less energy on earth, less resources on earth, higher prices everywhere, negative economic growth in the whole Western World, lower economic growth in the Emerging World and higher economic growth in the Energy Surplus Nations plus Africa.

This gap between supply and demand is not a future scenario, but is actually happening and growing since 2005. The gap is still relatively small, but, as one can see in Figure.1, it will become more wide year after year and will cause the logical attached price rises and supply interruptions.

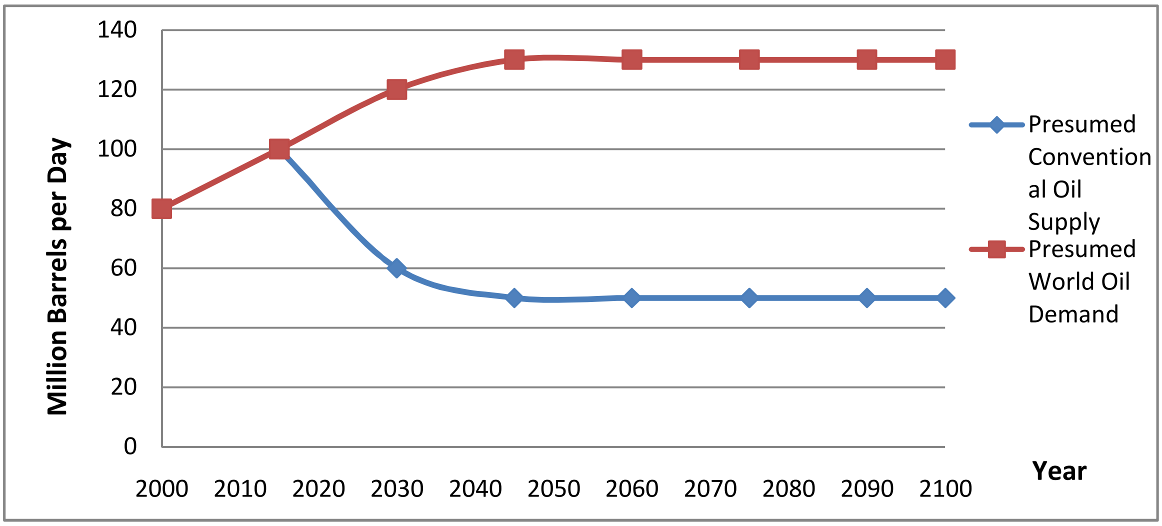
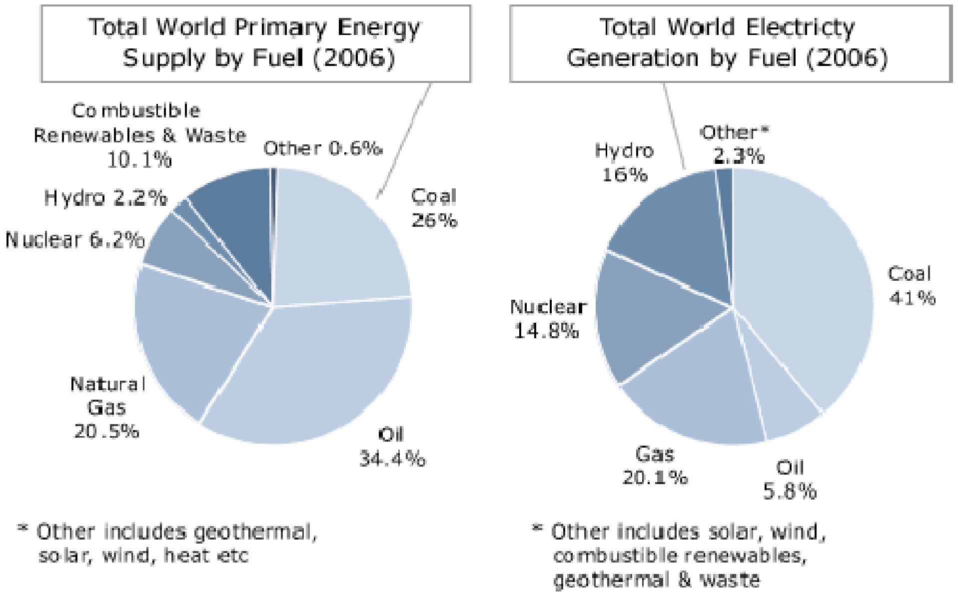


Figure 1.Present and Future Global Oil Demand and Supply [48]

The above mentioned environmental problems and oil shortage create the imperative need for the world economy to break loose from the oil dependence and move towards clean energy production. **Coal** is already widely used in energy generation and is the most abundant fossil fuel in the world. On an oil-equivalent basis, there is approximately twice as much recoverable coal in the world as oil and natural gas combined [IEA, 1999]; consequently, coal has been and will continue to be a major energy resource. With 41% of the world electricity generation being produced using coal as a fuel (2006 – Figure.2), it is clear that there cannot be total energy independence from fossil fuels. Thus, the environmentally friendlier use of fossil fuels and coal in particular is the challenge of the future.


Total World Primary Energy Supply by Fuel (2006)

Total World Electricty Generation by Fuel (2006)

* Other includes geothermal, solar, wind, heat etc

* Other includes solar, wind, combustible renewables, geothermal & waste

Figure 2. Total World Primary Energy Supply and Electricity Generation by Fuel - 2006 [36]

According to both the Intergovernmental Panel on Climate Change and the International Energy Agency, **Carbon Capture and Sequestration (CCS)** alone has the potential of reducing total greenhouse gas emissions by 20–30% by 2050. In other words, this technology could bring about a large part of the cuts needed to avoid irreversible climate change. CCS is a broad term that encompasses a number of technologies that can be used to capture CO_2 from point sources, such as power plants and other industrial facilities; compress it; transport it mainly by pipeline to suitable locations; and injects it into deep subsurface geological formations for indefinite isolation from the atmosphere.

Three main approaches can be used to capture CO_2 from Power Plants: Post – Combustion Capture, Pre – Combustion Capture and Oxy – Fuel Combustion. **Post – combustion capture** refers to the separation of CO_2 from the flue gas of a combustion process. Fuel sources can be any hydrocarbon, such as coal, natural gas, or oil. For coal plants, post-combustion capture is typically associated with subcritical pulverized coal (PC), supercritical pulverized coal (SCPC), ultra-supercritical pulverized coal (USCPC), and circulating fluidized bed (CFB) plants. **Pre-combustion capture** involves the generation of syngas (carbon monoxide plus hydrogen ($CO+H_2$)), followed by the shift reactions to convert the CO to CO_2.

CO_2 is then separated from hydrogen, and the hydrogen can be burned in a turbine or used as fuel in a heater. **Oxy-fuel combustion** involves the combustion of fuel in an oxygen-rich environment to dramatically increase the CO_2 concentration of the resulting flue gases. The increased CO_2 concentration (typically >80%) of the flue gas stream facilitates CO_2 separation. Oxyfiring produces lower emissions of nitrogen oxides (NO_x) compared to air-blown combustion. After combustion, the flue gas can be captured and compressed, although some cleaning to remove contaminants may be necessary before compression.

Pre-combustion capture is often associated with **Integrated Gasification Combined Cycle (IGCC) technology**. Most studies, suggest it is more cost-effective to use pre-combustion technologies with IGCC because the CO_2 can be captured at higher pressures compared to post combustion [IPCC 2005].

Integrated gasification combined-cycle (IGCC) systems combine a coal gasification unit with a gas fired combined cycle power generation unit. The first stage is the **coal gasification** process as mentioned above. The second stage includes the combustion of the clean gas in a conventional gas turbine producing electrical energy. The hot exhaust gas is used in a Heat Recovery Steam Generator (HRSG), producing steam which is expanded in a steam turbine producing electrical energy. In typical combined-cycle plants, about 65% of the electrical energy is produced by the gas turbine and 35% by the steam turbine.

Only some of the advantages of IGCC are the high thermal efficiency (up to 50%), lower rates of carbon dioxide emissions, small volume of solid wastes and feed stock flexibility.

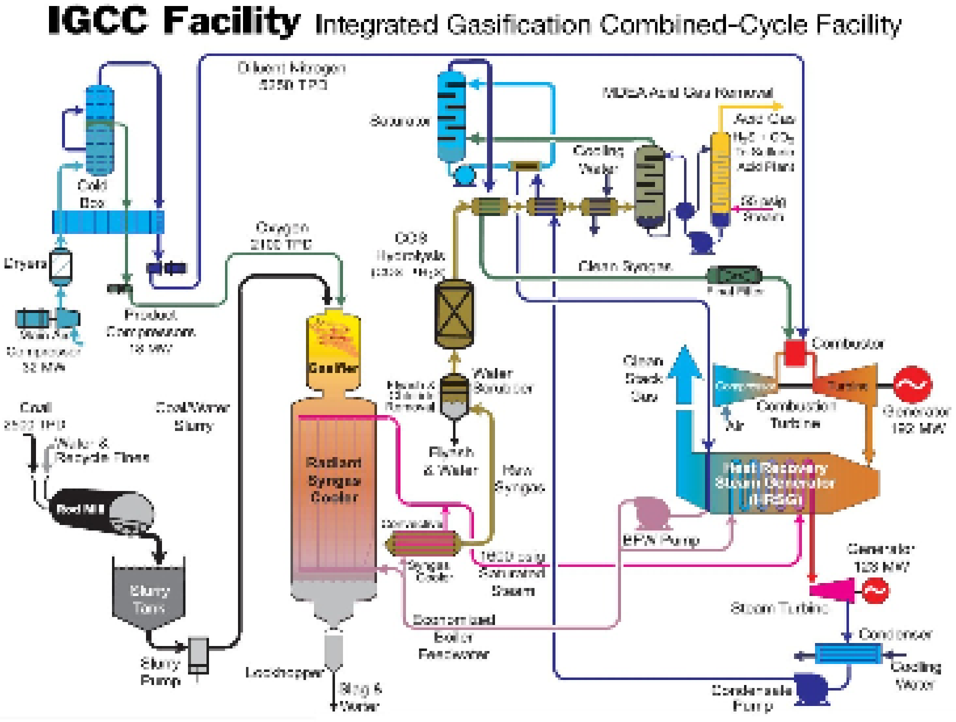


Figure 3. IGCC Diagram [55]

Because of the advantages of the IGCC power generation, the interest in the area of gasification process and gasification techniques is constantly increasing and it has also created the need of an approach in terms of **numerical simulation**. The benefits of such an approach can be translated as lower initial costs in the deployment of a possible gasification project and greater efficiency when operating due to operation in optimized conditions.

There has been a lot of scientific research in the area of numerical modeling of coal gasification and with many successful results. However there seems to be a lack of simulation data for gasification pressure conditions as high as 50 bar. The HotVeGas - HHV Project that has been launched at the Technical University of Munich (TUM) is aiming to explore gasification at such high pressures and high temperatures. The purpose of this diploma thesis is to contribute to the above project by modeling the gasification of coal with the use of the commercial CFD program ANSYS CFX. The results obtained refer to various pressure conditions from atmospheric to up to 50 bar and are analyzed from the standpoint of hydrogen production. The settings of the model can be easily adjusted and successfully predict the behavior of the gasification process in various input conditions which makes the model flexible and suitable for examining various combinations of initial conditions for the optimization of an actual gasifier. The model presented in this diploma thesis has proved to operate successfully but further accuracy improvement can be achieved in the future by comparing simulation results with experimental data.

2 Theoretic Background and Information

2.1 Coal

2.1.1 The Origin of Coal

Coal is a naturally occurring hydrocarbon that consists of the fossilized remains of buried plant debris that have undergone progressive physical and chemical alteration, called coalification, in the course of geological time. Coalification is the process of metamorphosis that takes place under conditions of raised temperature and pressure and results in the transformation of the original peat swamp through the progressive stages of brown coal (lignite), Subbituminous coals, bituminous coals, to anthracites and meta-anthracites. The level that a coal has reached in this coalification series is termed its ‘’rank’’.

Coal consists principally of carbon, hydrogen, oxygen and small amounts of sulfur and nitrogen and is mainly in the form of polycondenced aromatic rings. Carbon atoms included in these rings account for 70-80% of the total carbon present in the coal, for example, bituminous coals. The aromatic nature of coal increases with rank. Coal is usually found in conjunction with mineral matter, and it is this content together with rank that determines its commercial suitability as a fuel [1].

Basic Coal Analysis

These analyses do not yield any information on coal structure but do provide important information on coal behavior and are used in the marketing of coals. Three analyses are used in classifying coal, two of which are chemical analyses and one is a calorific determination. The chemical analyses include proximate and ultimate analysis. The proximate analysis gives the relative amounts of moisture, volatile matter, ash and indirectly, the fixed carbon contents of the coal. The ultimate analysis gives the amounts of carbon, hydrogen, nitrogen, sulfur and oxygen comprising the coal. The third important analysis, the calorific value, also known as heating value, is a measure of the amount of energy that a given quantity of coal will produce when burned.

Because moisture and mineral matter (or ash) are extraneous to the coal substance, analytical data can be expressed on several different bases to reflect the composition of as-received, air dried, or fully saturated coal or the composition of dry, ash-free (daf), or dry, mineral-matter-free (dmmf) coal.

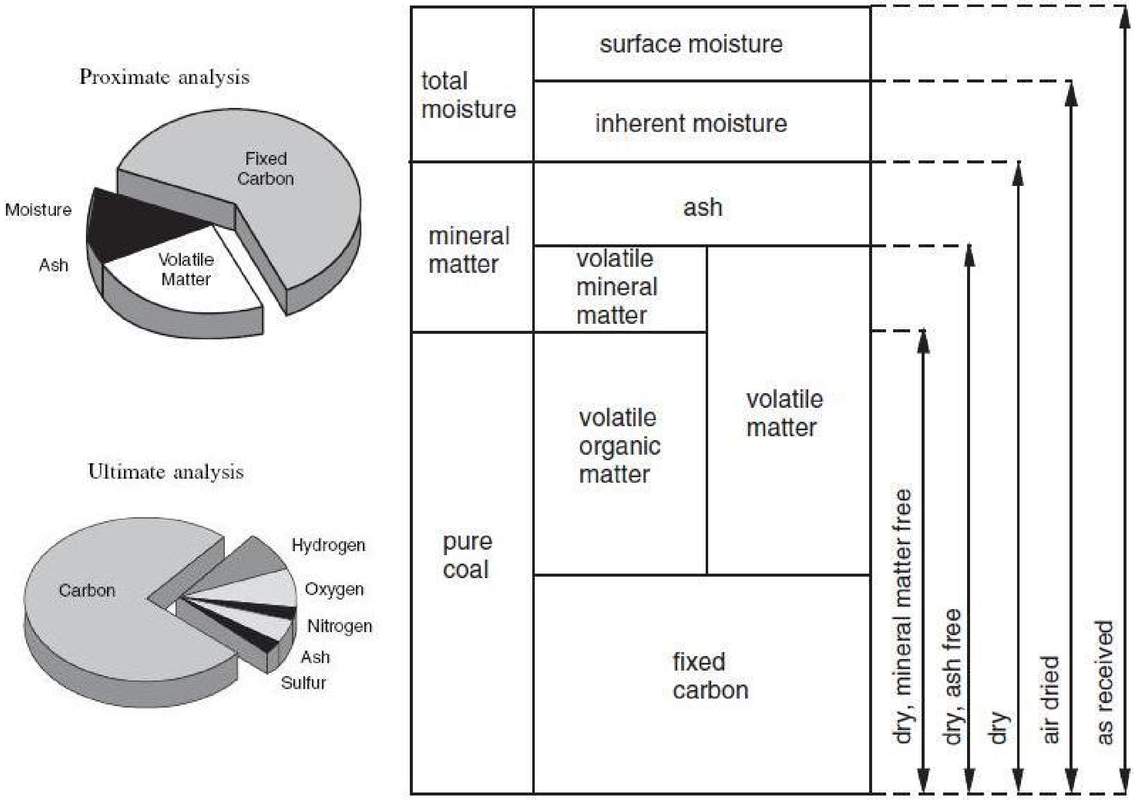


Figure 4. Proximate/Ultimate and other commonly used analysis bases [3]

The most commonly used bases in the various classification schemes can be described as follows:

- As-received – Data are expressed as percentages of the coal with the moisture. This category is also sometimes referred to as as-fired and is commonly used by the combustion engineer to monitor operations and for performing calculations as it is the whole coal that is being utilized.
- Dry basis (db) – Data are expressed as percentages of the coal after the moisture has been removed.
- Dry, ash-free (daf) – Data are expressed as percentages of the coal with the moisture and ash removed.
- Dry, mineral-matter-free (dmmf) – The coal is assumed to be free of both moisture and mineral matter, and the data are a measure of only the organic portion of the coal.
- Moist, ash-free (maf) – The coal is assumed to be free of ash but still contains moisture.
- Moist, mineral-matter-free (mmmf) - The coal is assumed to be free of mineral matter but still contains moisture.

Rank of Coal

The degree of coal maturation is known as the *rank* of coal and is an indication of the extent of metamorphism the coal has undergone. Rank is also a measure of carbon content as the percentage of fixed carbon increases with extent of metamorphism. Lignite and Subbituminous coals are referred to as being low in rank, while bituminous coals and anthracites are classified as high-rank coals. Note that the heating value increases with increasing rank but begins to decrease with semi-anthracitic and higher rank coals. This decrease in heating value is due to the significant decrease in volatile matter and it is also depicted in Figure.5 [3].

Class	***Group***	***Fixed Carbon (%dmmf)***	***Volatile Matter (% mmmf)***	***Calorific Value (KJ/Kg mmmf)***
I. Anthracitic	1.Meta-anthracite	≥98	< 2	
	2.Anthracite	92-98	2 - 8	
	3.Semianthracite	86-92	8 - 14	
II. Bituminous	1.Low volatile bituminous coal	78-86	14 - 22	
	2.Medium volatile bituminous coal	69-78	22 - 31	
	3.High volatile A bituminous coal	<69	> 31	≥32564
	4.High volatile B bituminous coal			30238-32564
	5.High volatile C bituminous coal			26749-30238
III. Sub - bituminous	1.Subbituminous A Coal			24423-26749
	2.Subbituminous B Coal			22097-24423
	3.Subbituminous C Coal			19306-22097
IV. Lignitic	1.Lignite A			14654-19306
	2.Lignite B			< 14654

Table 1. Coal Classification (ASTM) [1]

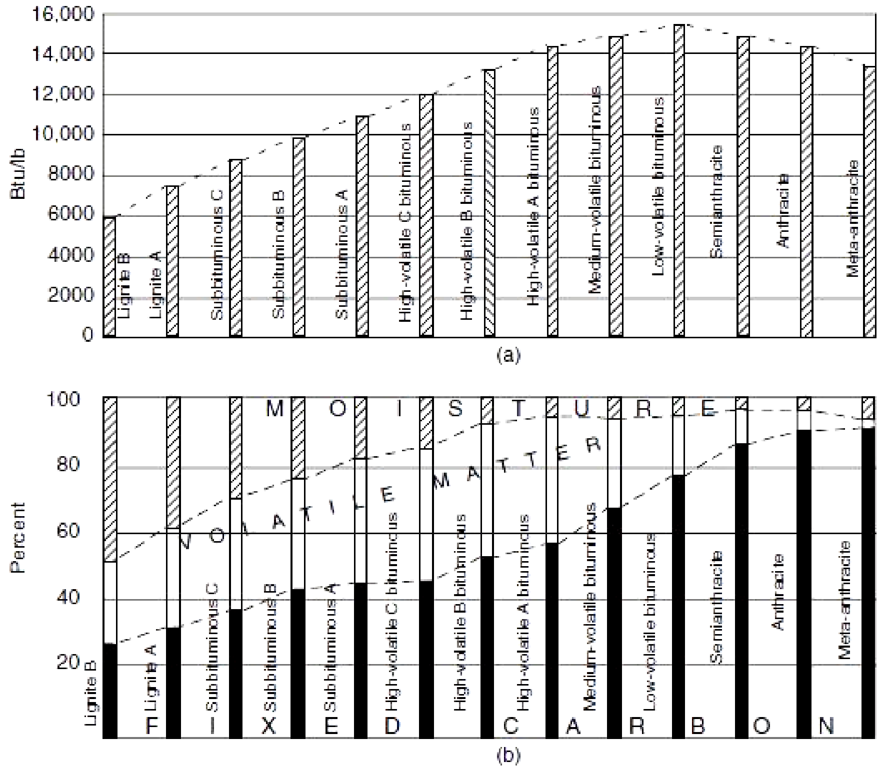


**Figure 5. Comparison of heating values (mmmf)
and proximate analyses of coal of different ranks.** [3]

Lignite is geologically very young (upward of around 40,000 years). It is brown and can be soft and fibrous, containing discernible plant material. It also contains large amounts of moisture (typically around 70%) and hence, it has low energy content (around 8 to 10 MJ/kg). As the coal develops it loses its fibrous character and darkens in color.

Black coal ranges from Cretaceous age (65 to 105 million years ago) to mid-Permian age (up to 260 million years ago). They are all black; some are sooty and still quite high in moisture (sub-bituminous coal). A common name for this coal in many parts of the world is "black lignite." Coals that get more deeply buried by other rocks lose more moisture and start to lose their oxygen and hydrogen; they are harder and shinier (e.g., bituminous coal). Typical energy contents are around 24 to 28 MJ/kg. These coals generally have less than 3% moisture, but some power stations burn coal at up to 30% ash.

Anthracite is a hard, black, shiny form of coal that contains virtually no moisture and very low volatile content. Because of this, it burns with little or no smoke and is sold as a "smokeless fuel." In general, coals only approach anthracite composition where bituminous coal seams have been compressed further by local crustal movements. Anthracites can have energy contents up to about 32 MJ/kg, depending on the ash content.

It is important to note that coal rank has little to do with quality. As a coal matures its ash content actually increases as a proportion because of the loss of moisture and volatiles. Lower rank coals may have lower energy contents, but they tend to be more reactive (i.e., they burn faster) because of their porosity and resultant higher surface area. [3]

2.1.2 The use of Coal

Coal has been used for massive energy production since the beginning of the industrialized society. Easy to get, large resources, a cheap and easy way to produce energy for the modern way of life. Although the use of oil and its products replaced many applications of coal, and made the world economy depending by it, the coal, with larger resources than oil (Table 2) never ceased to have an important place in the energy production field.

Fossil Resource	*Reserves*	*Resources*	*Additional Occurrences*	*TOTAL*
Conventional Oil	1100	1063		**2163**
Unconventional Oil	1340	2460	13370	17170
Conventional Natural Gas	1030	2050		3080
Unconventional Natural Gas	1410	1890	2840	6140
Hydrates			137500	137500
Coal	7350	17570	20860	**45780**
TOTAL	12230	25030	174570	211833

Table 2. Remaining World Fossil Fuel Reserves
(Billions of Barrels Equivalent – 2000) [44]

Coal is used as a solid fuel to produce electricity and heat through combustion. World coal consumption is about 6.2 billion tons annually. China produced 2.38 billion tons in 2006 and India produced about 447.3 million tons in 2006. 68.7% of China's electricity comes from coal. The USA consumes about 1.053 billion tons of coal each year, using 90% of it for generation of electricity [48]. The world in total produced 6.19 billion tons of coal in 2006.

When coal is used for electricity generation, it is usually pulverized and then burned in a furnace with a boiler. The furnace heat converts boiler water to steam, which is then used to spin turbines which turn generators and create electricity. The thermodynamic efficiency of this process has been improved over time. "Standard" steam turbines have topped out with some of the most advanced reaching about 35% thermodynamic efficiency for the entire process, which means 65% of the coal energy is waste heat released into the surrounding environment. Old coal power plants are significantly less efficient and produce higher levels of waste heat. About 40% of the world's electricity comes from coal [36].

2.2 Coal and Environment

2.2.1 Global warming

The detailed causes of the recent warming remain an active field of research, but the scientific consensus is that the increase in atmospheric greenhouse gases due to human activity caused most of the warming observed since the start of the industrial era, and the observed warming cannot be satisfactorily explained by natural causes alone. This attribution is clearest for the most recent 50 years, for which the most detailed data are available.

The greenhouse effect was theorized by Joseph Fourier in 1824 and was first investigated quantitatively by Svante Arrhenius in 1896. It is the process by which absorption and emission of infrared radiation by atmospheric gases warm a planet's lower atmosphere and surface.

2.2.2 Greenhouse Gases

Existence of the greenhouse effect as such is not disputed. Naturally occurring greenhouse gases have a mean warming effect of about 33 °C, without which Earth would be uninhabitable. On Earth, the major greenhouse gases are water vapor, which causes about 36 – 70 percent of the greenhouse effect (not including clouds); carbon dioxide (CO_2), which causes 9 – 26 percent; methane (CH_4), which causes 4 – 9 percent; and ozone, which causes 3 – 7 percent. The issue is how the strength of the greenhouse effect changes when human activity increases the atmospheric concentrations of some greenhouse gases.

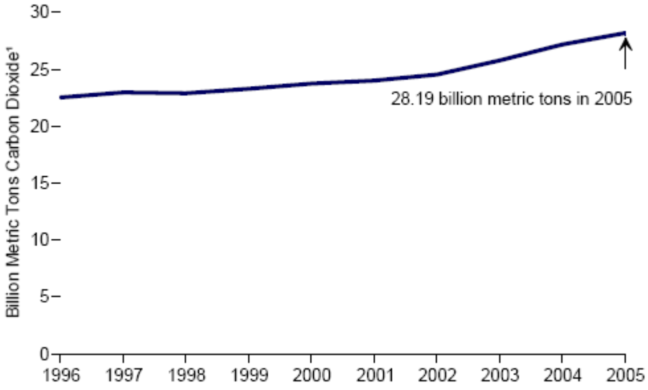


Figure 5. World Carbon Dioxide Emissions from Energy Consumption [48]

Human activity since the industrial revolution has increased the concentration of various greenhouse gases, leading to increased radiative forcing from CO_2, methane, tropospheric ozone, CFC's and nitrous oxide. Molecule for molecule, methane is a more effective greenhouse gas than carbon dioxide, but its concentration is much smaller so that its total radiative forcing is only about a fourth of that from carbon dioxide. Some other naturally occurring gases contribute small fractions of the greenhouse effect; one of these, nitrous oxide (N_2O), is increasing in concentration owing to human activity such as agriculture. The atmospheric concentrations of CO_2 and CH_4 have increased by 31% and 149% respectively since the beginning of the industrial revolution in the mid-1700s. These levels are considerably higher than at any time during the last 650,000 years, the period for which reliable data has been extracted from ice cores. From less direct geological evidence it is believed that CO_2 values this high were last attained 20 million years ago. Fossil fuel burning has produced approximately three-quarters of the increase in CO_2 from human activity over the past 20 years. Most of the rest is due to land-use change, in particular deforestation.

The present atmospheric concentration of CO_2 is about 385 parts per million (ppm) by volume. Future CO_2 levels are expected to rise due to ongoing burning of fossil fuels and land-use change. The rate of rise will depend on uncertain economic, sociological, technological, and natural developments, but may be ultimately limited by the availability of fossil fuels. The Intergovernmental Panel on Climate Change (IPCC) Special Report on Emissions Scenarios gives a wide range of future CO_2 scenarios, ranging from 541 to 970 ppm by the year 2100. Fossil fuel reserves are sufficient to reach this level and continue emissions past 2100, if coal, tar sands or methane clathrates are extensively used.

Inasmuch as the greenhouse effect is due to human activity, it is a forcing effect that is separate from forcing due to climate variability.

2.2.3 Clean Coal Technologies

Clean coal is an umbrella term used in the promotion of the use of coal as an energy source by emphasizing methods being developed to reduce its environmental impact. These efforts include chemically washing minerals and impurities from the coal, gasification, treating the flue gases with steam to remove sulfur dioxide, and carbon capture and storage (CCS) technologies to capture the carbon dioxide from the flue gas. These methods and the technology used are described as clean coal technology. Major politicians and the coal industry use the term "clean coal" to describe technologies designed to enhance both the efficiency and the environmental acceptability of coal extraction, preparation and use, with no specific quantitative limits on any emissions, particularly carbon dioxide.

It has been estimated that commercial-scale clean-coal power stations (coal-burning power stations with Carbon Capture and Sequestration - CCS) cannot be commercially viable and widely adopted before 2020 or 2025. This time frame is of concern to environmentalists, because, according to the Stern report (released on October 30, 2006 by economist Lord Stern of Brentford for the British government and discusses the effect of climate change and global warming on the world economy) there is an urgent need to mitigate greenhouse gas emissions and climate change. That is why research on the field of CCS must be immediate, thorough and efficient so that the solutions proposed on the matter of lower greenhouse gas emission can be successful and with long-term viability.

2.3 Carbon Capture and Sequestration (CCS)

Carbon capture and sequestration (CCS) is an approach to mitigating global warming based on capturing carbon dioxide (CO_2) from large point sources such as fossil fuel power plants and storing it instead of releasing it into the atmosphere. Although CO_2 has been injected into geological formations for various purposes, the long term storage of CO_2 is a relatively untried concept.

The capture and sequestration of carbon dioxide are critical enabling technologies to significantly reduce CO_2 emissions while still allowing fossil fuels to meet the energy demands of today. The merit of CCS systems is the reduction of CO_2 emissions by up to 90%, depending on plant type. Carbon capture and sequestration begins with the separation and capture of CO_2 from power plant flue gas and other stationary CO_2 sources. At present, this process is costly and energy intensive, accounting for the majority of the cost of sequestration. CCS applied to a modern conventional power plant could reduce CO_2 emissions to the atmosphere by approximately 80-90% compared to a plant without CCS. Capturing and compressing CO_2 requires much energy and would increase the fuel needs of a coal-fired plant with CCS by 25% - 40%. These and other system costs are estimated to increase the cost of energy from a new power plant with CCS by 21-91%. These estimates apply to purpose-built plants near a storage location: applying the technology to preexisting plants or plants far from a storage location will be more expensive. On Table 3 the results of techno-economic studies made on applying CCS technology to IGCC are presented.

IGCC Case Study CO_2 Capture	**Thermal Efficiency (%)**		**Efficiency Loss (%)**	**Increase of Cost of Electricity (%)**
	Without CCS	With CCS		
90% [22]	38.1	32.9	13.6	45
85% (Shell Gasification Technology) [23]	43.1	34.5	20	32.2 – 33.6
85% (GE Gasification Technology) [23]	38	31.3	17.1	23.9 – 24.4
80% [24]	41	34.4	16	~ 30
85% (Puertollano based data) [25]	43.9	33.5	23.7	~ 39

Table 3. Efficiency Loss and Increase of COE due to CCS

Storage of the CO_2 is envisaged either in deep geological formations, in deep ocean masses, or in the form of mineral carbonates. In the case of deep ocean storage, there is a risk of greatly increasing the problem of ocean acidification, a problem that also stems from the excess of carbon dioxide already in the atmosphere and oceans. Geological formations are currently considered the most promising sequestration sites, and these are estimated to have a storage capacity of at least 2000 Gt CO_2 (currently, 30 Gt per year of CO_2 is emitted due to human activities). A general problem is that long term predictions about submarine or underground storage tightness are very difficult and uncertain. The CO_2 could leak from the storage and finally appear in the atmosphere. IPCC estimates that the economic potential of CCS could be between 10% and 55% of the total carbon mitigation effort until year 2100.

The construction of the first pilot-scale CCS power plant started on May 29, 2006, by the Swedish company Vattenfall. The plant is located near the existing lignite fired 1600 MW power plant in Schwarze Pumpe, Germany. The pilot plant has been in operation from the middle of 2008. The initial testing program will run for three years. The plant is scheduled to operate for at least 10 years in the hope of answering questions about technological feasibility and economic efficiency. [56]

- Carbon Capture methods from Power Plants

Three main approaches are used to capture CO_2 from power plants:

- Post-combustion capture,
- Oxy-fuel combustion and
- Pre-combustion capture.

2.3.1 Post – combustion capture

Post-combustion capture requires the addition of a capture system (to separate the CO_2 from the other flue gas components and concentrate the CO_2) and a compression system (to compress the CO_2 and prepare it for transport). Leading post-combustion capture technologies also require significant cleaning of the flue gas before the capture device. In particular, sulfur levels have to be low (less than 10 parts per million (ppm) and possibly lower) to reduce corrosion and fouling of the system. Figure 6 shows a sample block diagram for post-combustion capture from a power plant. As shown in Figure 6, after leaving the boiler, flue gas is cleaned with a scrubber that removes sulfur dioxide (SO_2) and a device that removes particulate matter (PM). The diagram shows the use of limestone slurry for this purpose, suggesting use of wet flue gas desulphurization (FGD). While wet FGD would not be a required component, it might be needed to reduce the sulfur content to the required level. Also, note that the flue gas cleanup area would include a device for PM collection. The flue gas then enters an absorption column (represented by the CO_2 capture box) that contains the amine solution. As the flue gas contacts the amine in the absorption column, the CO_2 is absorbed into the amine solution. The flue gas then exits the stack, and the amine solution is sent to a stripping column, where the CO_2 is removed from the amine solution through an increase in the solution temperature. The amine is recycled and sent to the absorption tower, while the CO_2 is cooled, dried, and compressed to a supercritical fluid. Besides the use of an amine solution (chemical absorption into solution), the options for post-combustion capture include physical adsorption with a solvent (ionic liquids) or a sorbent (metal organic frameworks), membrane separation from the gas (membrane/amine hybrids or enzymatic CO_2 processes), and cryogenic separation by distillation or freezing [NETL 2007]. Chemical absorption into a solution is currently the preferred approach for separating CO_2 from flue gases at low concentrations, such as those associated with power plants. There is considerable experience using amines, such as MEA, for the separation of CO_2 during natural gas processing and in the development of food-grade CO_2. While expensive, it is currently considered a commercial post-combustion capture process [MIT 2007].

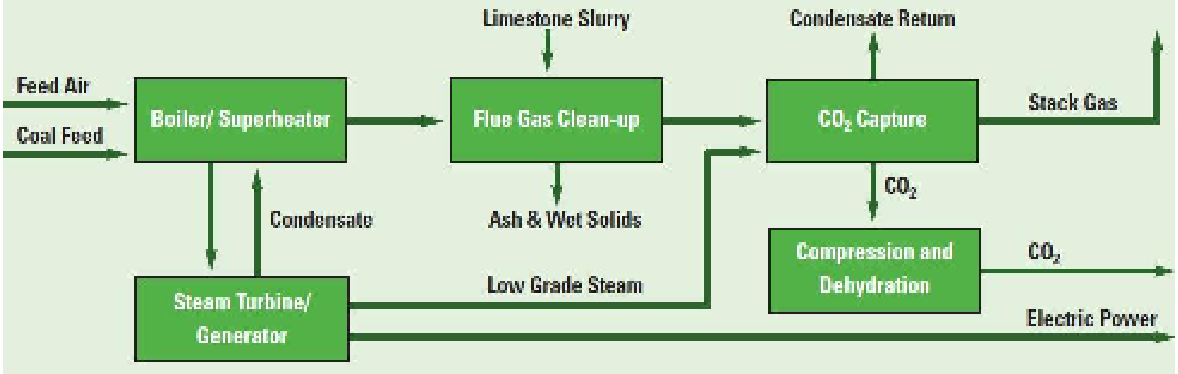


Figure 6. Post-combustion capture from a pulverized coal-fired power plant [54]

2.3.2 Oxy – fuel Combustion

Oxy-fuel combustion involves the combustion of fossil fuels in an oxygen-rich environment (nearly pure oxygen mixed with recycled exhaust gas), instead of air. Combustion under these conditions reduces the formation of nitrogen oxides, so that the gas leaving the combustion zone is primarily CO_2 and is easier to separate and remove. As shown in Figure 7 an air separation unit supplies oxygen to the boiler where it mixes with the recycled exhaust gas. After combustion, the gas stream can be cleaned of PM, nitrogen oxides, and sulfur. After condensing out the water, the flue gas has a CO_2 concentration that is high enough to allow direct compression. However, the compressed flue gas may have to be further cleaned

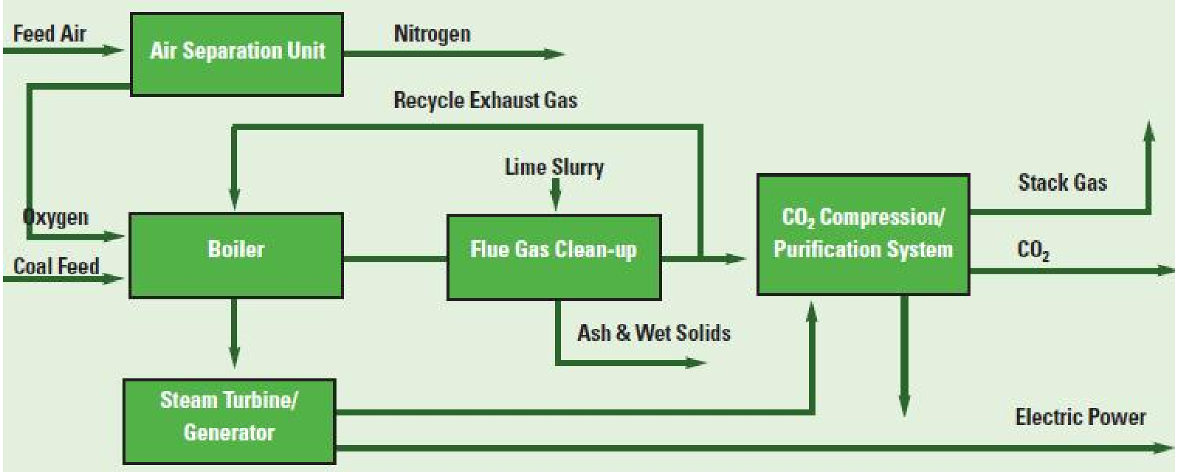


Figure 7.Oxy-fuel combustion with capture [54]

of co-constituents to reach the same purity as the compressed CO_2 resulting from post-combustion capture [MIT 2007]. As of 2008, oxy-fuel power plants are in the early stages of development with pilot-scale construction currently underway in North America and an operating power plant running on a test basis in Schwarze Pumpe, Germany.

2.3.3 Pre – Combustion Capture

Pre-combustion capture involves the removal of CO_2 after the coal is gasified into syngas, but before combustion in an IGCC unit. As shown in Figure 8, the first step involves gasifying the coal. Then, a water-gas shift reactor is used to convert carbon monoxide in the syngas and steam to CO_2 and hydrogen. This increases the concentration of CO_2, improving CO_2 capture efficiency and increasing the amount of carbon (in the form of CO_2) that can be removed using this process. The CO2 is removed using either a chemical or a physical solvent, such as Selexol™, and is compressed. The hydrogen is combusted in a turbine to generate electricity [MIT 2007]. While both IGCC and pre-combustion CO_2 capture technologies are considered available, only four gigawatts of IGCC power plants have been built worldwide as of the end of 2007 [IPCC 2005]. None of the existing IGCC plants have the technologies needed to capture the CO_2.

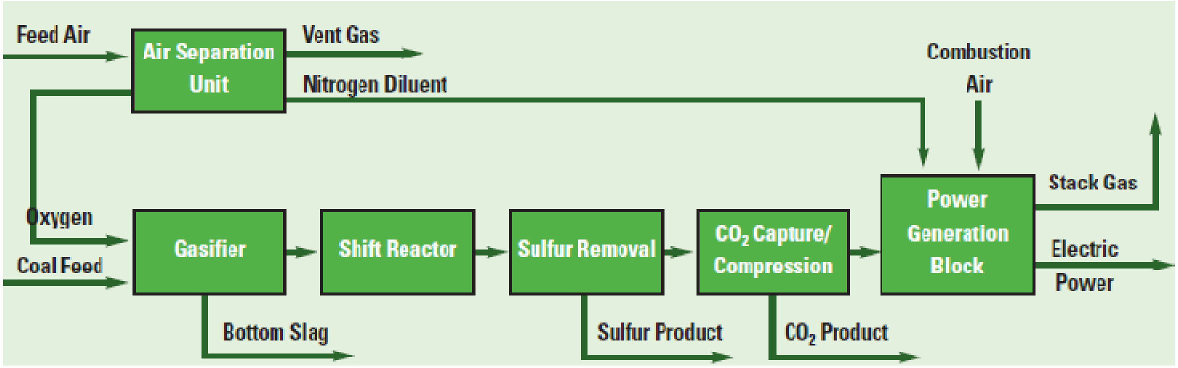


Figure 8. Pre-combustion capture on an IGCC power plant [54]

2.4 Gasification and Pyrolysis

2.4.1 The History of Gasification

The production of combustible gas from coal and carbon-containing materials is already an old technology. So-called dry distillation or pyrolysis (heating of feedstock in absence of oxygen, resulting in thermal decomposition of the fuel into volatile gases and solid carbon) was first practiced on a commercial scale in 1812 by a gas company in London.

The first commercial gasifier of the up-draft type for continuous air-blown gasification of solid fuels was installed in 1839, yielding what is currently known as "producer gas”. Gasifiers were then developed for different fuels and industrial power and heating applications up to the 1920s, when oil fueled systems gradually took over systems fueled by producer gas. In anticipation of unreliable petroleum supplies, compact gasifier systems like the more advanced down-draft type, for automotive applications were developed in Europe between 1920 and 1940 but they were largely decommissioned after a while, when inexpensive liquid fuels became widely available.

The energy crisis of the 1970s brought renewed interest in gasification. The technology was perceived as a relatively cheap indigenous alternative for small-scale industrial and utility power generation in developing countries that suffered from high petroleum prices prevailing on the world market and that had sufficient sustainable biomass resources. In the beginning of the 1980s, at least 10 (mainly European) manufacturers offered small-scale wood and charcoal-fueled power plants (of up to approximately 250 kW), and at least four developing countries (Philippines, Brazil, Indonesia and India) started gasifier implementation programs based on locally developed technologies. Dozens, perhaps hundreds, of biomass gasification systems were installed through donor-financed projects and local entrepreneurs in a large number of developing countries.

In Western countries, coal gasification systems attracted interest during the 1980s as an alternative to using natural gas and oil in (dedicated) heat applications. Technological development mainly applied to fluidized-bed gasification systems for coal in the range of 10 to 100MW. Currently, development of gasification systems is directed to production of electricity and heat in advanced gas-turbine-based cogeneration units.

Gasification looks simple in principle and many types of gasifiers have been developed. The production of gaseous fuel from a solid fuel – with attractive properties such as easy handling and combustion that produce little excess air and low levels of contaminants (and possibly can be used in internal combustion engines) - makes gasification very appealing [20] .

2.4.2 Gasification and Pyrolysis processes

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, or biomass, into a combustible gas by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam. The resulting gas mixture consists of carbon monoxide, hydrogen and some methane and carbon dioxide and it is called synthesis gas or syngas and is itself a fuel. Gasification is a very efficient method for extracting energy from many different types of organic materials, and also has applications as a clean waste disposal technique. Gasification uses heat and pressure (and possibly steam) to convert any raw material (feedstock) that contains carbon, into synthesis gas. Sometimes pure oxygen is used, in a process called “oxygen-gasification”, or air can be used in “air-gasification" and then the product gas also contains nitrogen. Steam can be added to the oxidant stream to increase the amount of hydrogen in the gas produced; alternatively, water can be added as a liquid when the coal is injected in the form of coal-water slurry. Carbon monoxide and hydrogen are colorless, odorless, highly flammable gases that can be used to produce electricity, chemicals, pure hydrogen, and liquid transportation fuels. Gasification systems are also being used increasingly to turn feedstocks, such as coal into useful chemical products.

Gasification can also be applicable to materials that are not otherwise useful fuels, such as biomass or organic waste. In addition, the high-temperature combustion refines out corrosive ash elements such as chloride and potassium, allowing clean gas production from otherwise problematic fuels.

Gasifying fossil fuels is currently widely used on industrial scales to generate electricity. However, almost any type of organic material can be used as the raw material for gasification, such as wood, biomass, or even plastic waste. Thus, gasification may be an important technology for renewable energy. Finally, gasification is also used industrially in the production of ammonia and synthetic liquid fuels, but also to produce electricity from fossil fuels such as coal, using Integrated Gasification Combined Cycle (IGCC). IGCC is also a more efficient method of CO_2 capture as compared to conventional technologies. There is also the possibility of producing methane and hydrogen for fuel cells.

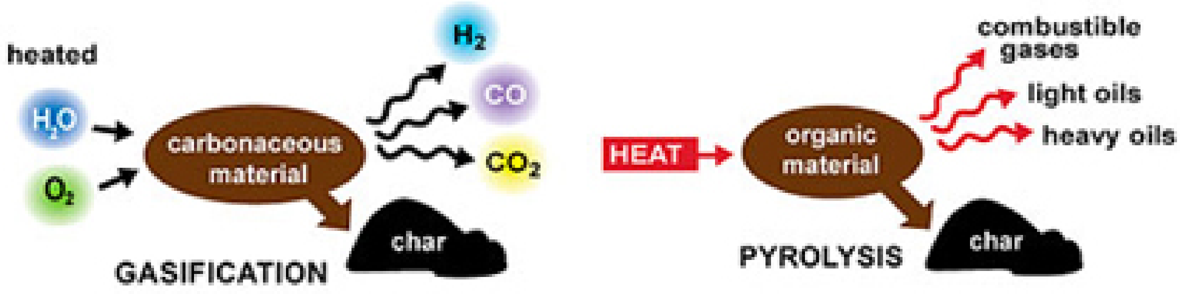


Figure 9. Gasification and Pyrolysis [50]

The **pyrolysis** (or devolatilization) process occurs as the particles of a carbonaceous material heat up. Pyrolysis is the chemical decomposition of organic materials by heating in the absence of oxygen or any other reagents, except possibly steam. Due to the high temperature and the small amounts of oxygen, volatiles are released and char is produced, resulting in up to 70% weight loss for coal. The process is dependent on the properties of the carbonaceous material and determines the structure and composition of the char, which will then undergo gasification reactions.

2.4.3 Gasification reactions

Gasification relies on chemical processes at elevated temperatures >700°C, which distinguishes it from biological processes such as anaerobic digestion that produce biogas. The coal gasification reactions occur when coal is heated with oxygen and usually some steam in a gasification reaction chamber. A typical bituminous coal has 77-90% carbon and contains 10-30% volatile matter, and it is convenient to discuss coal gasification mainly in terms of the reaction of carbon with a suitable gas. The main reactions which take place in a gasification system are:

Pyrolysis of coal and its break-up into char and volatile matter.

Coal → char + volatiles …………………Endothermic reaction……………(R 2.1)

Heterogeneous reactions of the char (carbon) produced with gasifying agent, steam or volatile matter.

Oxidation of char

$C + \frac{1}{2} O_2 \rightarrow CO$ ………………………… $\Delta H^o_{298} = - 123$ KJ / mol……….. (R2.2)

$C + O_2 \rightarrow CO_2$ ……………………………$\Delta H^o_{298} = - 406$ KJ / mol……….. (R2.3)

Boudouard reaction

$C + CO_2 \rightarrow 2CO$ …………………………$\Delta H^o_{298} = + 159.7$ KJ / mol……… (R2.4)

Char – steam reaction

$C + H_2O \rightarrow CO + H_2$…………………… $\Delta H^o_{298} = - 118.9$ KJ / mol……… (R2.5)

Hydrogenation

$C + 2H_2 \rightarrow CH_4$………..…………………$\Delta H^o_{298} = - 88.4$ KJ / mol……… … (R2.6)

Gasification of the char or carbon with carbon dioxide (Boudouard reaction) is usually the prime process together with the partial oxidation steps. The Boudouard reaction is endothermic and, for a given carbon in the absence of catalyst, takes place several orders of magnitude slower than the $C – O_2$ reaction at the same temperature. The reaction proceeds very slowly at temperatures below 1000K, and is inhibited by its product, CO. If there is a significant amount of steam present, then reaction with carbon takes place. This reaction has high activation energy and the rate is proportional to the steam partial pressure.

Gas Phase reactions among the gases already produced inside the gasifier.

Oxidation reactions

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$……………………………$\Delta H^o_{298} = -242$ KJ / mol……….. (R2.7)

$CO + \frac{1}{2} O_2 \rightarrow CO_2$ ……………………….$\Delta H^o_{298} = -283$ KJ / mol……….. (R2.8)

$CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2H_2$………………..$\Delta H^o_{298} = -35.7$ KJ / mol……….. (R2.9)

Water – gas shift reaction

$CO + H_2O \leftrightarrow CO_2 + H_2$……………… $\Delta H^o_{298} = -40.9$ KJ / mol……….… (R2.10)

Steam reforming reaction

$CH_4 + H_2O \leftrightarrow CO + 3H_2$…………….. $\Delta H^o_{298} = +206$ KJ / mol……….. (R2.11)

Although all of the above reactions were presented as if they take place each one in a discrete phase from another, actually, they all occur simultaneously.

There is a balance between the extent of combustion and gasification processes that is controlled by the products required and therefore the chosen stoichiometry and the reaction temperature and pressure. By a change in conditions the products can include more CO and H_2, and this is achieved when power generation is the objective. High temperatures and pressures favor CO and H_2 production while low temperatures favor a higher methane content.

There are endothermic reactions, i.e., require heat in order to proceed. Therefore, the heat required for these desired reactions is supplied by the complete or partial combustion of a small proportion of the coal in oxygen or air.

Two gas-phase reactions are important for the final gas composition. The water-gas shift reaction has influence on the CO/H_2 ratio, which can be important if the gas is for use in synthesis. The shift reaction increases the amount of hydrogen in the gases. Because of the hydrogen in the gas phase, hydrogenation of carbon also occurs, so that the gasifier gases also contain some methane. Methane is also produced from the reverse steam reforming reaction (reaction of carbon monoxide and hydrogen). The methanation reaction increases the calorific value of the gas, but is very slow except at high pressure and in catalytic-bed reactions. The shift and methanation reactions are particularly important for substitute natural gas (SNG) production.

2.4.4 The advantages of gasification

Gasification is the cleanest coal-based power system available today. There are five main advantages or benefits of gasification technology.

Feedstock flexibility:

Gasification can produce syngas not only from coals having a wide range of heat values but also from low-value carbon feedstock's such as petroleum coke ("pet coke"), high-sulfur fuel oil, municipal wastes, and biomass. This flexibility increases the economic value of these resources and lowers costs by providing industry with a broader range of feedstock options.

Product flexibility:

The syngas produced by gasification can be converted into many valuable products, ranging from electricity and steam to liquid fuels, basic chemicals, and hydrogen. Integration of multiple products gasification into industrial applications increases opportunities for added revenues since plant operations can focus on the most lucrative products, provides economies of scale associated with production of multiple commodities and increases opportunities for added revenues.

Near-zero emissions:

Gasification systems can meet the strictest environmental regulations pertaining to emissions of sulfur dioxide (SO_2), particulate matter, and toxic compounds other than coal contaminates such as mercury, arsenic, selenium, cadmium, etc.. Further, gasification provides an effective means of capturing and storing or sequestering carbon dioxide (CO_2), a greenhouse gas. The carbon dioxide produced during gasification is present at much higher concentrations and at higher pressures than in streams produced from conventional combustion, making them easier to capture. The vision is to convert synthesis gas into pure hydrogen using the water - gas shift reaction and use the hydrogen as an ultra-clean fuel with an exhaust gas of nothing but water.

High efficiency:

Gasification can be integrated with other technologies for advanced power generation, particularly combustion turbines and eventually solid oxide fuel cells. The resulting systems are highly efficient, squeezing more value from each pound of feedstock. Systems using advances in gasification and related components can achieve efficiencies of up to 60 percent, compared with an efficiency limit of 40 percent for conventional plants.

2.4.5 Syngas

The Synthesis Gas (or Syngas) is the product of the gasification process. It consists of Hydrogen and Carbon Monoxide but it can contain also other gases such us Carbon Dioxide, Methane and water.

The composition of the synthesis gas is not specified and depends on a great amount of factors. The type of coal gasified, the gasification temperature and pressure, the oxidation mean of the process can make the concentration values of gases that syngas consists of, vary.

Minor constituents in the feedstock are converted to such products as hydrogen sulfide, ammonia, and ash/slag (mineral residues from coal).

It is one of the advantages of gasification that using the syngas is potentially more efficient than direct combustion of the original fuel because it can be combusted at higher temperatures or even in fuel cells, so that the thermodynamic upper limit to the efficiency defined by Carnot's rule is higher. Syngas may be burned directly in internal combustion engines, used to produce methanol and hydrogen, or converted via other chemical processes into synthetic fuel.

Syngas can be used for heat production or for mechanical / electrical power generation in technologies such as the Integrated Gasification Combined Cycle (IGCC). Like any other gaseous fuel, it enables a good control over power levels when compared to solid fuels, paving the way for more efficient and cleaner operation.

Syngas has a heating value of about 4 - 15 MJ/m^3 , which is three to eight times lower than that of natural gas. [49]

2.5 The Integrated Gasification Combined Cycle (IGCC)

The IGCC technology is relatively new in connection with power generation. It uses a combined cycle format with a gas turbine driven by the combusted syngas, while the exhaust gases are heat exchanged with water/steam to generate superheated steam to drive a steam turbine. Using IGCC, more of the power comes from the gas turbine. Typically 60-70% of the power comes from the gas turbine with IGCC, compared with about 20% using Pressurized Fluidized Bed Combustion (PFBC).

Coal gasification takes place in the presence of a controlled 'shortage' of air/oxygen, thus maintaining reducing conditions. The process is carried out in an enclosed pressurized reactor, and the product is the synthesis gas. The product gas is cleaned and then burned with either oxygen or air, generating combustion products at high temperature and pressure. The sulphur present mainly forms H_2S but there is also a little COS. The H_2S can be more readily removed than SO_2. Although no NO_x is formed during gasification, some is formed when the fuel gas or syngas is subsequently burned. IGCC plants can be configured to facilitate CO_2 capture (CCS Technology). The syngas is 'shifted' using steam to convert CO to CO_2, which is then separated for possible long-term sequestration. The emissions of particulates, NO_x and SO_2 from IGCC units is expected to meet, and possibly to better, all current standards. On most units, sulphur is produced in elemental form as a by-product. Residues may include both ash and slag, depending on the gasification system used.

2.5.1 Types of Gasifiers

The gasifier is the main system component of the gasification process. It is a robust pressure vessel where air (or oxygen), steam, and a suitable fuel are brought together and heated, stimulating controlled thermal and chemical reactions that convert the feedstock to syngas.

The feedstock is prepared and fed to a gasifier in either a dry form or as slurry (mixed with water). In the gasifier, the feedstock reacts with steam and air or oxygen (O_2) at high temperature and pressure in a reducing (oxygen-starved) atmosphere. These conditions produce the syngas.

The high temperature in the gasifier converts the inorganic materials left behind by gasification and fuses them into a glassy material, generally referred to as slag. The slag has the consistency of coarse sand. It is chemically inert and may have a variety of uses in the construction and building industries.

Depending on its type, a gasifier may operate at temperatures up to 1800ºC, and pressures up to 70 atmospheres. When the feedstock particles enter the gasifier and move through its zones they undergo three thermal and chemical processes – the first two in very rapid succession and the third more slowly: Pyrolysis, Oxidation (controlled burning) and Gasification/Reduction. This type of reaction is endothermic, and slag is left as a waste product. The net result of all of the chemical reactions inside a gasifier is that gasification is exothermic.

Three types of gasifier are currently available for commercial use:

- Fixed-bed gasifiers (counter-current and co-current)
- Fluidized-bed gasifiers and
- Entrained-flow gasifiers.

Fixed (Moving) Bed		Fluidized Bed	Entrained Flow	
Dry Ash Gasifiers	Slagging Gasifiers	IDGCC	Slagging Gasifiers	
		ABGC	Slurry Feed	Dry Feed
		BHEL		Hitachi
BHEL	BGL	HTW	GE (Texaco)	SCGP
Lurgi		KRW	E – Gas	MHI
		Transport	BBP	BBP
		Reactor		Prenflo

Table 4. Coal gasification technology suppliers [10]

2.5.1.1 Fixed – bed gasifiers

Gasification processes based on **fixed beds** have been used since the start of the twentieth century for producing a lean gas using air gasification. Ash removal from fixed-grate systems was a problem, and this was solved by using rotating grates. Generally, the fixed-bed dimensions are typically 4 - 5 m in depth and 4 m in diameter.

The **counter-current fixed bed ("up draft") gasifier** consists of a fixed bed of carbonaceous fuel (e.g. coal or biomass) through which the "gasification agent" (steam, oxygen and/or air) flows in counter-current configuration. The ash is either removed dry or as a slag. The slagging gasifiers require a higher ratio of steam and oxygen to carbon in order to reach temperatures higher than the ash fusion temperature. The nature of the gasifier means that the fuel must have high mechanical strength and must be non-caking so that it will form a permeable bed, although recent developments have reduced these restrictions to some extent. The throughput for this type of gasifier is relatively low. Thermal efficiency is high as the gas exit temperatures are relatively low. However, this means that tar and methane production is significant at typical operation temperatures, so product gas must be extensively cleaned before use or recycled to the reactor.

In the updraft gasifier, fuel is fed at the top and descends though gases rising through the reactor. In the upper zone a drying process occurs, below which pyrolysis is taking place. Following this, the material passes through a reduction zone

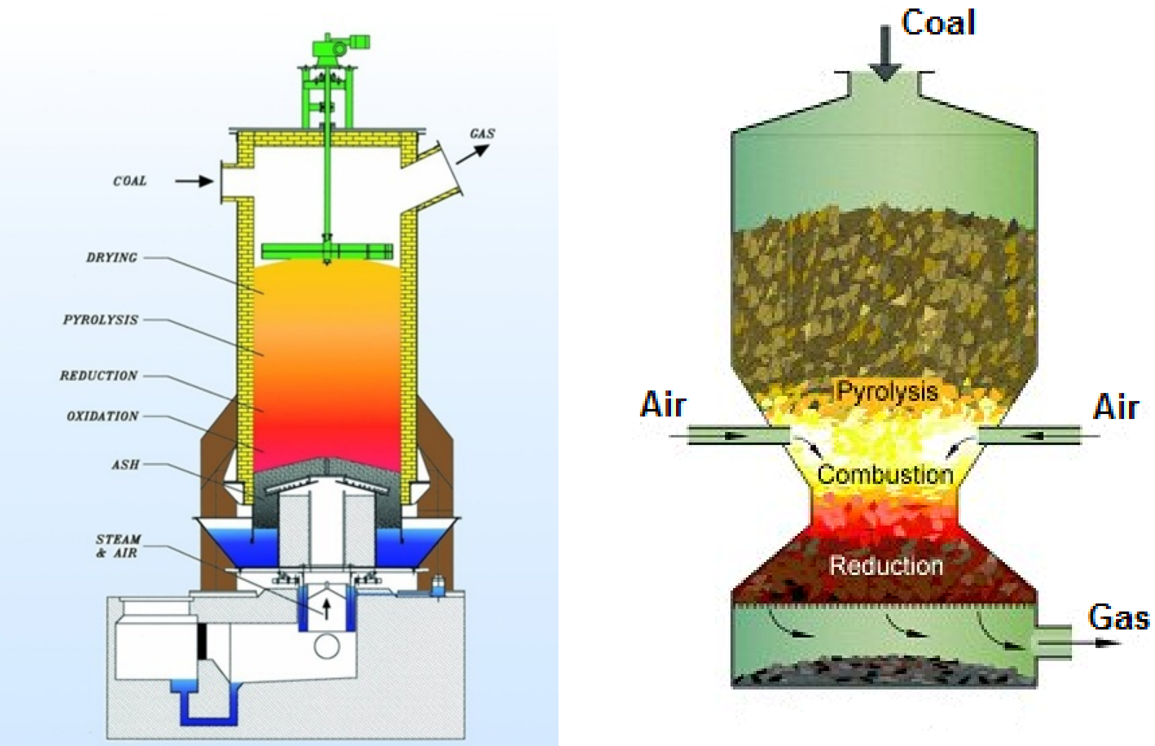


Figure 10. Counter-Current (left) and Co-Current fixed bed Gasifier (right) [52], [53]

(gasification) and in the zone above the grate an oxidation process is carried out (combustion). To supply air for the combustion process and steam for the gasification process, moist hot air is supplied at the bottom of the reactor. Combustible gas at a low temperature (because of the evaporation of moisture in the drying zone) is discharged at the top of the reactor, and inert ash from the heat-generating combustion process is extracted from the reactor bottom through a water lock.

The **co-current fixed bed ("down draft") gasifier** is similar to the counter-current type, but the gasification agent gas flows in co-current configuration with the fuel (downwards, hence the name "down draft gasifier"). Heat needs to be added to the upper part of the bed, either by combusting small amounts of the fuel or from external heat sources. The produced gas leaves the gasifier at a high temperature, and most of this heat is often transferred to the gasification agent added in the top of the bed, resulting in energy efficiency on the same level with the counter-current type. Since all tars must pass through a hot bed of char in this configuration, tar levels are much lower than the counter-current type.

Fixed (moving) – bed Technologies

BGL: The British Gas/Lurgi (BGL) coal gasifier is a dry-fed, pressurized, fixed-bed, slagging gasifier. The reactor vessel is water cooled and refractory lined. Each gasifier is provided with a motor-driven coal distributor/mixer to stir and evenly distribute the incoming coal mixture. Oxygen and steam are introduced into the gasifier vessel through sidewall-mounted tuyeres (lances) at the elevation where combustion and slag formation occur. The coal mixture (coarse coal, fines, briquettes, and flux), which is introduced at the top of the gasifier via a lock hopper system, gradually descends through several process zones. Coal at the top of the bed is dried and devolatilized. The descending coal is transformed into char, and then passes into the gasification (reaction) zone. Below this zone, any remaining carbon is oxidized, and the ash content of the coal is liquified, forming slag. Slag is withdrawn from the slag pool by means of an opening in the hearth plate at the bottom of the gasifier vessel. The slag flows downward into a quench chamber and lock hopper in series. The pressure differential between the quench chamber and gasifier regulates the flow of slag between the two vessels. Product gas exits the gasifier at approximately 570°C through an opening near the top of the gasifier vessel and passes into a water quench vessel and a boiler feed water (BFW) preheater designed to lower the temperature to approximately 150°C. Entrained solids and soluble compounds mixed with the exiting liquid are sent to a gas-liquor separation unit. Soluble hydrocarbons, such as tars, oils, and naphtha, are recovered from the aqueous liquor and recycled to the top of the gasifier or reinjected at the tuyeres.

Lurgi: The Lurgi dry ash gasifier is a pressurized, dry ash, moving-bed gasifier. Sized coal enters the top of the gasifier through a lock hopper and moves down through the bed. Steam and oxygen enter at the bottom and react with the coal as the gases move up the bed. Ash is removed at the bottom of the gasifier by a rotating grate and lock hopper. The countercurrent operation results in a temperature drop in the reactor. Temperatures in the combustion zone near the bottom of the gasifier are in the range of 1100 °C, whereas gas temperatures in the drying and devolatization zone near the top are approximately 260 to 540°C. The raw gas is quenched with recycled water to condense tar. A water jacket cools the gasifier vessel and generates part of the steam to the gasifier. Sufficient steam is injected to the bottom of the gasifier to keep the temperature below the melting temperature of ash.

BHEL: The gasification media, a mixture of air and steam, is fed through a grate, which also enables ash removal. A gas cooler is used to recover part of the sensible heat of the gas produced and superheat steam for the gasifier. Further gas cooling as well as tar condensation are done by water quenching. Particulates are removed with a Venturi scrubber. A pilot plant has been operated for more than 5500 hours (1100 hours as IGCC), with two types of coals having high ash contents: Singareni coal with an ash content of 27 to 35% and North Karanpura coal with an ash content of 40%. The North Karanpura coal was also tested in the Lurgi pilot-scale plant at the Indian Institute of Chemical Engineering (IICT) under the same gasification conditions. It resulted in a better performance of the BHEL gasifier (calorific value and cold gas efficiency), due mainly to the larger scale of the gasifier. However, the availability of the plant was affected by the poor performance of the raw gas cooler due to tar deposition and choking. A direct contact quench was subsequently designed to replace the gas cooler and overcome that problem. The performance of the moving-bed gasifier was also compared to that of a pressurized fluidized-bed gasifier later developed by BHEL at the Trichy unit in Hyderabad in India. Moving-bed gasifiers produce tar-laden gas, which make the recovery of the sensible heat of the raw gas difficult. They also need coals with a certain particle size (5 to 30 mm). They produce large effluents containing tars and phenolic acids, requiring elaborate effluent treatment. For these reasons, BHEL decided to develop the fluidized-bed technology for the processing of Indian coals. A 6.2 MWe IGCC plant was developed by BHEL at the Trichy unit in 1988, as part of a research program for the development of gasification of Indian coals for the production of electricity. The gasification process was based on a moving-bed technology developed in-house, after experience on a Lurgi dry ash bed gasifier (pilot-scale 24 ton/day) was gained at the Indian Institute of Chemical Engineering at Hyderabad and at CFRI at Dhanbad. The gasifier is a 2.7 m diameter, 14 m high jacketed moving-bed gasifier with a coal throughput of 150 tpd. Crushed coal of 5 to 40 mm size with an ash content of about 35% is the design feedstock for the gasifier, which is operating at 1 MPa pressure.

2.5.1.2 Fluidized – bed gasifiers

A **Fluidized bed** is formed when a quantity of a solid particulate substance (usually present in a holding vessel) is placed under appropriate conditions to cause the solid/fluid mixture to behave as a fluid. This is usually achieved by the introduction of pressurized fluid through the particulate medium. This results in the medium then having many properties and characteristics of normal fluids; such as the ability to free-flow under gravity, or to be pumped using fluid type technologies.

In a fluidized bed reactor, the fuel is fluidized in oxygen and steam or air. The reactor is operated at a constant temperature, usually below the ash fusion temperature, thereby avoiding agglomeration and clinker formation and defluidizes the bed. As coal particles are consumed or fragmented during gasification, the smaller particles are entrained with the hot raw gas as it leaves the reactor; these char particles are recovered and recycled to the reactor.

Fluidized-bed gasifiers may differ in ash conditions, being run either dry or agglomerated. The ash is removed dry or as heavy agglomerates that defluidize. In **dry ash gasifiers** the temperatures are relatively low, so the fuel must be highly reactive; conventional dry ash operation has traditionally operated on low-rank coals. The agglomerated ash operation involves slightly higher temperatures, and improves the ability of the process to gasify high-rank coals efficiently. Fuel throughput is higher than for the fixed bed, but not as high as for the entrained flow gasifier. The conversion efficiency can be rather low due to elutriation of carbonaceous material. Recycle or subsequent combustion of solids can be used to increase conversion. Fluidized-bed gasifiers are most useful for fuels that form highly corrosive ash that would damage the walls of slagging gasifiers.

The immediate forerunner is the original Winkler process, which is a fluidized-bed system that uses steam and air or oxygen at atmospheric pressure.

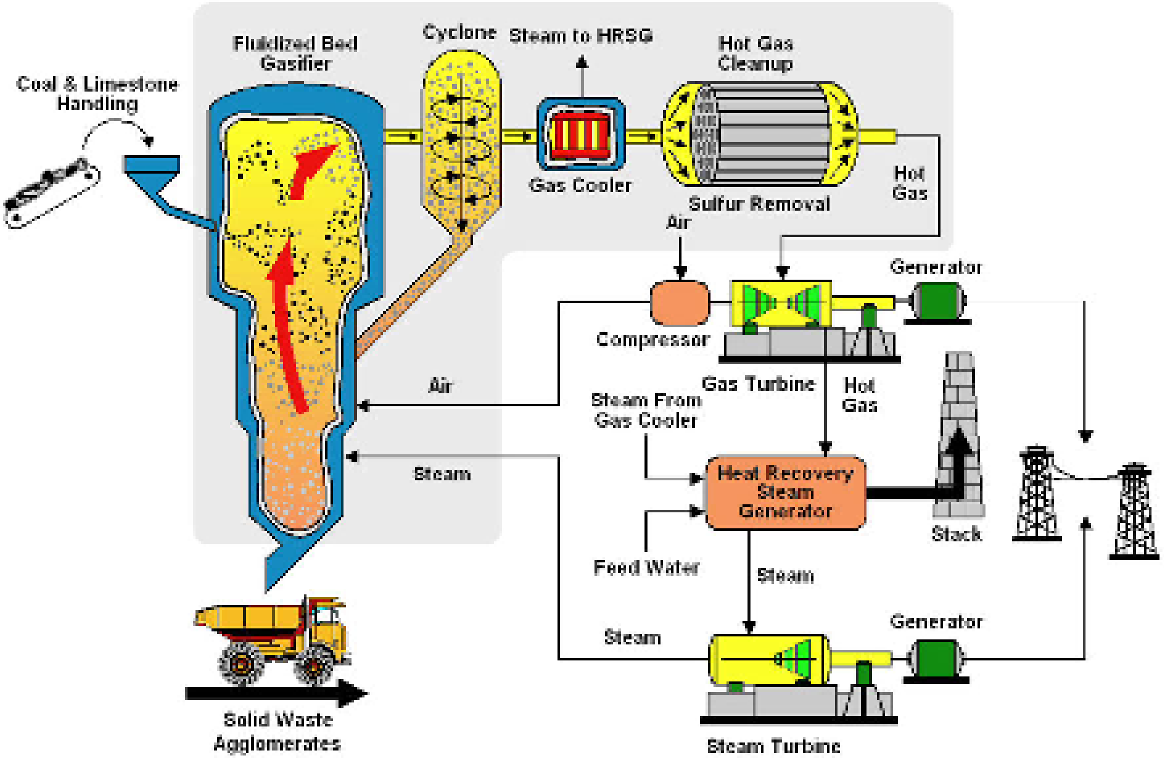


Figure 11. Fluidized Bed Gasifier - used in an Integrated Cycle [39]

Fluidized – bed Technologies

HTW: The High Temperature Winkler (HTW) process was first developed by Rheinbraun in Germany to gasify lignite for the production of a reducing gas for iron ore. The gasifier consists of a refractory-lined pressure vessel equipped with a water jacket. Feedstocks are pressurized in a lock hopper, which is located below the coal storage bin and then pneumatically conveyed to a coal bin. The conveying gas is then filtered and recirculated. Coal in the receiving bin is then dropped via a gravity pipe into the fluidized bed, which is formed by particles of ash, semi-coke, and coal. The gasifier is fluidized from the bottom with either air or oxygen/steam, and the temperature of the bed is kept at around 800°C, below the fuel ash fusion temperature. An additional gasification agent is introduced at the freeboard to decompose, at higher temperature (900 to 950°C), undesirable byproducts formed during gasification. The operating pressure can vary from 1 to 3 MPa, depending on the use of the syngas. The raw syngas produced is passed through a cyclone to remove particulates and then cooled. Solids recovered in the cyclones are reinjected into the gasifier, and dry ash is removed at the bottom via a discharge screw. The syngas cooling system has been the subject of study as to whether to use a water-cooled or a firetube syngas cooler. The main reason was that the existing water-cooled syngas cooler was facing fouling and corrosion problems. A conventional water scrubber system was originally used for gas cleaning but due to blockages, fouling, corrosion, and also the high operating cost of the system, Rheinbraun decided to develop a hot gas filtration system. A hot gas ceramic candle unit formed of 450 candles was developed and operated for 15,000 hours. The HTW technology manufactured by Rheinbraun was successfully applied for the synthesis of chemicals (methanol) from lignite at Berrenrath, Germany, between 1986 and 1997. The plant was shut down at the end of 1997 as, at the time, the process was no longer considered to be economically viable. Another commercial plant has been operating in Finland since 1988, essentially with peat for the production of ammonia. A 140 ton coal/day pressurized HTW gasification plant was also commissioned and built at Wesseling, Germany, in 1989, to supplement research and development of the HTW technology for coal use and particularly to study its future application to an IGCC process for power generation. The plant was designed for a maximum thermal capacity of 36 MW and was operated for 3 years either as an air-blown or an oxygen-blown gasification plant with pressures up to 2.5 MPa. A wide range of coals was tested in the Wesseling plant, including brown coals and a high-volatile bituminous coal (Pittsburgh No. 8). The Wesseling plant provided the operational data required to design a potential 300 MW commercial IGCC power plant (KoBra), which was finally never built. However, there is presently a project to develop a 400 MW IGGC plant based on the HTW technology (two units) to replace 26 existing Lurgi moving beds at Vresova in the Czech Republic. The new HTW plant (80 ton/hour coal and pressures up to 3 MPa) should operate on Czech lignite and will benefit from years of research and development at the Wesseling and Berrenrath plants. In order to adapt the HTW technology to the Czech lignite and also to the pre-existing Vresova IGCC plant (coal grinding plant, air separation unit, wastewater treatment, and steam turbine), tests were performed by Rheinbraun in an HTW bench-scale gasification unit and compared to results obtained with other coals in the same benchscale unit and in a demonstration plant.

IDGCC: The Integrated Drying Gasification Combined Cycle (IDGCC) technology was specifically developed for the gasification of high-moisture, low-rank coals by Herman Research Pty Limited in Morwell, Australia. The gasifier is a 5 MW air-blown pressurized fluidized-bed pilot plant that is fed with coal from an integrated drying process. The feed coal is pressurized in a lock hopper system and then fed into the dryer, where it is mixed with the hot gas leaving the gasifier. The heat in the gas is used to dry the coal, while the evaporation of water from the coal cools down the gas without the need of expensive heat exchangers. The gasifier operates at 900°C under 2.5 MPa air pressure. Chars and ash are collected at the bottom of the gasifier and from a ceramic filter and burnt in a separate boiler. The final ash product is similar to that from a conventional low-rank boiler. A wide range of low-rank coals could be processed in the IDGCC, with only small changes in the operating conditions. Coals containing high levels of sulfur can be processed with sorbents, such as limestone or dolomite, directly injected into the bed. This would obviate the need for additional cooling of the gas to 40°C for sulfur removal from the very high-moisture syngas. The extra cooling would have led to a very large energy loss from water condensation and reduced mass energy for the gas turbine. It is expected that the IDGCC could handle coals with lower moisture content and higher ash content. As the IDGCC plant is based on a fluidized-bed gasification technology, it is then not recommended, as in most of the fluidized bed technologies, for coals with relatively low reactivities and coals with low ash melting points. When looking at environmental considerations and particularly at the concept of CO_2 removal and H_2 production, the IDGCC, which produces a very moist syngas, can provide the water for the shift reaction without robbing or much reduced robbing of the steam cycle and may have potential for future development. It was reported that the IDGCC process is more efficient and as a consequence more environmentally friendly (lower CO_2 emission) than conventional processes, and would be just slightly less efficient than an Australian black coal IGCC process.

KRW: Coal and limestone, crushed to below 6 mm, are transferred from feed storage to the KRW fluidized-bed gasifier via a lock hopper system. Gasification takes place by mixing steam and air (or oxygen) with the coal at a high temperature. The fuel and oxidant enter the bottom of the gasifier through concentric high-velocity jets, which ensure thorough mixing of the fuel and oxidant and of the bed of char and limestone that collects in the gasifier. After entering the gasifier, the coal immediately releases its volatile matter, which burns rapidly, supplying the endothermic heat of reaction for gasification. The combusted volatiles form a series of large bubbles that rise up the center of the gasifier, causing the char and sorbent in the bed to move down the sides of the reactor and back into the central jet. The recycling of solids cools the jet and efficiently transfers heat to the bed material. Steam, which enters with the oxidant and through a multiplicity of jets in the conical section of the reactor, reacts with the char in the bed, converting it to fuel gas. At the same time, the limestone sorbent, which has been calcined to CaO, reacts with H_2S released from the coal during gasification, forming CaS. As the char reacts, the particles become enriched in ash. Repeated recycling of the ash-rich particles through the hot flame of the jet melts the low-melting components of the ash, causing the ash particles to stick together. These particles cool when they return to the bed, and this agglomeration permits the efficient conversion of even small particles of coal in the feed. The velocity of gases in the reactor is selected to maintain most of the particles in the bed. The smaller particles that are carried out of the gasifier are recaptured in a high efficiency cyclone and returned to the conical section of the gasifier, where they again pass through the jet flame. Eventually, most of the smaller particles agglomerate as they become richer in ash and gravitate to the bottom of the gasifier. Since the ash and spent sorbent particles are substantially denser than the coal feed, they settle to the bottom of the gasifier, where they are cooled by a counter-flowing stream of recycled gas. This both cools and classifies the material, sending lighter particles containing char back up into the gasifier jet. The char, ash, and spent sorbent from the bottom of the gasifier flow to the fluid-bed sulfator, where both char and calcium sulfide are oxidized. The CaS forms $CaSO_4$, which is chemically inert and can be disposed of in a landfill. Most of the spent sorbent from the gasifier contains unreacted CaO. Sulfur released from burning residual char in the sulfator is also converted to $CaSO_4$. Pinon Pine in Nevada is the only large-scale coal-based IGCC plant (100 MWe) that is using the KRW technology, and it is also the only one that was designed with a 100% hot gas cleanup. The demonstration plant, owned by Sierra Pacific Resources and sponsored by the U.S. DOE, has had numerous problems. The gasifier had 18 start-ups, and all of them failed due to equipment design. Successes in the project included operation of the combined cycle portion of the plant at 98% availability, efficient removal by the hot gas filter of particulates from the syngas and production of a good quality syngas for only 30 hours since the first syngas was produced in 1998. Sierra Pacific Resources, which owns the Pinon Pine power plant, was going to be sold to WPS Power Development, but the sale has been suspended by the state of Nevada, which placed a moratorium on the sale of power plants in the state.

ABGC: The Air-Blown Gasification Cycle (ABGC) is a hybrid system that was developed at pilot scale (0.5 ton/hour coal capacity) by the former Coal Technology Development Division of British Coal. The gasifier is based on a spouted bed design and is operated at pressures up to 2.5 MPa and a temperature between 900 and 1000°C. Coal fed in the gasifier produces a gas with a low calorific value of around 3.6 MJ/m^3 . Sorbents such as limestone are also injected into the gasifier to retain up to 95% of the sulfur originally present in coal. Syngas is first cleaned in a cyclone, then cooled to around 400°C and cleaned by a ceramic filter, to be finally burned and expanded through a gas turbine. Only 70 to 80% of the fuel is gasified, and partially gasified char and other solid residues (fly ash and sulphided sorbent residues) produced in the gasifier are then transferred to an atmospheric pressure circulating fluidized-bed combustor (CFBC) operating at a temperature of about 1000°C. Heat generated by the combustion of the char supplies a steam cycle used to drive a steam turbine to supplement the electricity generation. The ABGC process is forecast to have an efficiency of about 46 to 48%. The ABGC technology was later purchased by Mitsui Babcock Energy Limited (MBEL), which produced in collaboration with GEC Alsthom and Scottish Power PLC a design of a demonstration plant while being supported by the European Commission under the THERMIE program. A wide range of UK coals and international steam coals were studied for use in the ABGC. A laboratory at Imperial College of Science Technology and Medicine in London studied the impact of several coal characteristics on the gasification reactivity of some international traded coals in bench-scale reactors that could mimic the behavior of single coal particles in the ABGC. Coal characteristics studied included coal maceral composition and coal mineral matter composition.

BHEL: A 168 ton coal/day capacity air-blown pressurized fluidized-bed gasifier IGCC pilot plant (6.2 MWe) was built at Hyderabad, India, following previous gasification tests in an 18 ton coal/day capacity IGCC fluidized-bed gasifier pilot plant and in a 150 ton coal/day moving bed IGCC pilot plant. The plant consists of a refractory lined reactor with a 1.4 m inside diameter in the bed, expanding to a 2 m inside diameter at the upper section of the gasifier. Crushed coal (6 mm size or below) is injected into the system via a lock hopper and a rotary coal feeder and then pneumatically transported into the gasifier with a portion of the air used by the plant. The dry granular ash produced during gasification is withdrawn from the bottom of the gasifier through a water-cooled screw extractor and is discharged periodically through an ash lock system. Three refractory cyclones operating in series are used for primary gas cleaning. Fines collected in the first two cyclones can be recycled in the gasifier but there is also the possibility to collect the cyclone fines, without recycling, through a lock hopper. The gasifier operates at a temperature of 1000°C and pressure of 1.3 MPa to generate a coal gas with a net calorific value of 9.8 MJ/kg. The 168 ton coal/day demonstration plant was commissioned in 1996 and has since undergone a series of tests in standalone and in IGCC mode, operating for a total of 1200 hours until the year 2000. The plant is designed for the gasification of Indian coals with a high ash content of up to 42%.

Transport Reactor:
The Kellogg Transport Gasifier is a circulating-bed reactor concept that uses finely pulverized coal and limestone. The gasifier is currently in development, which may lead to a commercial design. It is expected that the small particle size of the coal and limestone will result in a high level of sulfur capture. Additionally, the small particle size will increase the throughput compared to a KRW gasifier, thereby potentially reducing the required number of gasifier trains (or the gasifier size) and the cost. The Transport Gasifier is conceptually envisioned as consisting of a mixing zone, a riser, cyclones, a standpipe, and a non-mechanical valve. Oxidant and steam are introduced at the bottom of the gasifier in the mixing zone. Coal and limestone are introduced in the upper section of the mixing zone. The top section of the gasifier discharges into the disengager or primary cyclone. The cyclone is connected to the standpipe, which discharges the solids at the bottom through a non-mechanical valve into the transport gasifier mixing zone at the bottom of the riser. The gasifier system operates by circulating the entrained solids up through the gasifier riser, through the cyclone, and down through the standpipe. The solids reenter the gasifier mixing zone through the non-mechanical valve. The steam and oxidant jets provide the motive force to maintain the bed in circulation and oxidize the char as it enters the gasifier mixing zone. The hot gases react with coal/char in

the mixing zone and riser to produce gasification products. The gas and entrained solids leaving the primary cyclone pass through the secondary cyclone to provide final de-entrainment of the solids from the gas. The solids separated in the secondary cyclone fall through the dipleg into the standpipe. A solids purge stream is withdrawn from the standpipe for solids inventory maintenance. The gas leaving the secondary cyclone passes through a gas cooler, which reduces the gas temperature from about 1040°C to 600°C.

2.5.1.3 Entrained flow gasifiers

The **entrained-flow gasification** processes were derived for the petroleum refining and chemical industry. The products need to have the correct proportion of CO/H_2 dependent on the application. Generally, equilibrium considerations indicate that as the temperature becomes higher, the amount of CO increases and the amount of methane decreases. Thus the amount of CO_2 and H_2 resulting from water-gas reaction increases as the temperature rises, and likewise from the Boudouard reaction. Thus, reactors operating at high temperature – with oxygen and high pressure – produce gases suitable for synthesis or for power generation.

In **entrained flow gasifiers**, the fine coal particles can be fed either dry (normally using nitrogen as transport gas) or wet (carried in water slurry). Some gasifiers use two-stage feeding to improve the thermal efficiency and reduce both the sensible heat in the raw gas and the oxidant requirements. Depending upon the method of coal feeding, dry or wet slurry, the entrained-flow gasifiers can accept almost any type of coal. This is also due to the high operating temperatures and because the coal particles are well separated from one another. The high temperatures and pressures (typically, such gasifiers work at pressures up to 35 bar and at the highest temperature of all the other gasifier types) mean that a higher throughput can be achieved, however thermal efficiency is somewhat lower as the gas must be cooled before it can be cleaned with existing technology. The high temperatures also mean that tar and methane are not present in the product gas; however the oxygen requirement is higher than for the other types of gasifiers.

All entrained flow gasifiers remove the major part of the ash as a slag as the operating temperature is well above the ash fusion temperature. A smaller fraction of the ash is produced either as a very fine dry fly ash or as a black colored fly ash slurry. Some fuels, in particular certain types of biomasses, can form slag that is corrosive for ceramic inner walls that serve to protect the gasifier outer wall. However some entrained bed type of gasifiers do not possess a ceramic inner wall but have an inner water or steam cooled wall covered with partially solidified slag. These types of gasifiers do not suffer from corrosive slags. Some fuels have ashes with very high ash fusion temperatures. In this case mostly limestone is mixed with the fuel prior to gasification. Addition of a little limestone will usually suffice for the lowering the fusion temperatures. The fuel particles must be much smaller than for other types of gasifiers. This means the fuel must be pulverized, which requires somewhat more energy than for the other types of gasifiers. By far the most energy consumption related to entrained bed gasification is not the milling of the fuel but the production of oxygen used for the gasification.

Entrained Flow Technologies

Hitachi: This coal gasification technology is based on an oxygen-blown entrained flow gasifier, where the majority of experience has been gained in a 150 ton coal/day unit. The gasifier is a water-cooled tube that is lined by a high-temperature-resistant castable. Pulverized coal is pneumatically transported by nitrogen to the gasifier, where it is injected into the gasifier chamber through two types of burners at a pressure of 2.5 MPa. The two sets of burners are installed tangentially to the gasifier sidewall, allowing a spiral flow of coal and oxygen from the upper stage to the lower stage and making particle residence times much longer than those of a gas stream. Enough oxygen is fed to the lower burner to melt the slag. Molten slag solidifies on the gasifier wall as a first layer, and subsequent molten slag flows over the layer of the solidified slag to the slag tap hole at the bottom of the gasifier; it is quenched with water and finally removed via a lock hopper. Coal fed to the upper burners is reacted at a lower temperature with a smaller amount of oxygen; it is then gasified and converted to reactive char. The char moves down along the spiral gas flow and mixes with high-temperature gas in the lower portion of the gasifier, where gasification proceeds further. The raw gas produced together with the fly ash and the remaining char particles go up toward the exit of the gasifier. They enter a syngas cooler, where they are cooled to 450°C prior to going through a cyclone and a filter that retain most of the fly ash and the char particles, which are finally reinjected into the gasifier by pneumatic transport under nitrogen. The syngas goes successively through a water scrubber to remove halides and is desulfurized to be cleaned enough to comply with the strict tolerance limits of fuel cells.

SCGP: The Shell Coal Gasification Process (SCGP) can operate on a wide variety of feedstocks. It consists of three principal stages: 1. Gasification (Partial Oxidation), in which the feedstock is converted to syngas in the presence of oxygen and a moderating agent (steam) in a refractory-lined gasification reactor. 2. Syngas Effluent Cooler (SEC), in which high-pressure steam is generated from the hot syngas leaving the reactor 3. Carbon removal, in which, residual carbon and ash are removed from the syngas in a two-stage water scrubbing unit. The Shell gasifier is a dry-feed, pressurized, entrained slagging gasifier. Feed coal is pulverized and dried with the same type of equipment used for conventional pulverized coal boilers. The coal is then pressurized in lock hoppers and fed into the gasifier with a transport gas by dense-phase conveying. The transport gas is usually nitrogen; however, product gas can be used for synthesis gas chemical applications, where nitrogen in the product gas is undesirable. The oxidant is preheated to minimize oxygen consumption and mixed with steam as a moderator prior to feeding to the burner. The coal reacts with oxygen at temperatures in excess of 1400°C to produce principally hydrogen and carbon monoxide with little carbon dioxide. Operation at elevated temperatures eliminates the production of hydrocarbon gases and liquids in the product gas. The high temperature gasification process converts the ash into molten slag, which runs down the refractory-lined water wall of the gasifier into a water bath, where it solidifies and is removed through a lock hopper as a slurry in water. Some of the molten slag collects on the cooled walls of the gasifier to form a solidified protective coating. The crude raw gas leaving the gasifier at 1400 to 1650°C contains a small quantity of unburned carbon and about half of the molten ash. To make the ash non-sticky, the hot gas leaving the reactor is partially cooled by quenching with cooled recycle product gas. Further cooling takes place in the waste heat recovery (syngas cooler) unit, which consists of radiant, superheating, convection, and economizing sections, where high-pressure superheated steam is generated before particle removal. The first commercial IGCC plant using the Shell Coal Gasification Process (SCGP) is Buggenum in the Netherlands, which was built in 1993. The plant achieves an overall efficiency of 43%, which could be increased to over 50% if using the most recent gas turbines. The Buggenum design processes coal with natural gas as backup. The plant can process up to 2000 ton/day of fuel. A demonstration plant (220 ton/day) at Oil Deer Park Manufacturing complex in Houston completed tests proving the ability of the SCGP to gasify more diverse types of coals (220 ton/day of bituminous coals or 365 ton/day of high-moisture, high-ash lignite) before being shut down in 1991. Any coal that can be milled to the right size and pneumatically transported can be gasified in the Shell entrained flow gasifier. Some adjustments have to be made in order to keep the SCGP performances optimal when changing coal. Bituminous coals require, in most cases, steam injection and oxygen/MAF (moisture- and ash-free) coal ratios from 0.85 to 1.05 for producing a syngas with a CO/H_2 ratio of 2.2 to 2.4 and 1 to 2.5% CO_2. Sub-bituminous coals and lignite normally do not require steam injection and can be operated with oxygen/MAT coal ratio between 0.8 and 0.9, producing syngas with some 3 to 5% CO_2 and a CO/H_2 ratio of 2.0 to 2.2. Anthracites require a higher oxygen/MAF coal ratio of 1.0 to 1.1 and a higher steam/oxygen ratio of 0.15 to 0.3, and they produce a syngas with similar CO_2 contents as bituminous coal (1 to 2.5% CO_2, but a higher CO/H_2 ratio of 2.4 to 2.6). The ash content of a coal has an impact on the performance of the SCGP process in terms of efficiency, as slag forms part of the insulation of the wall of the gasifier and then prevents excessive heat loss during the gasification reaction. A new Integrated Gasification Combined Cycle (IGCC) project based on the SCGP technology, was also proposed to be built at Sulcis in Sardinia, Italy. It was planned to have similar characteristics as the Buggenum plant. The Sulcis plant has been designed to gasify 5000 ton/day blends of local coal (high-sulfur, high-ash sub-bituminous coal) and imported LHV coals. A large IGCC demonstration plant is also planned to be built at Yantai Power plant in Shandong province in China. Technical prefeasibility studies were carried out in 1994–95. Development prospects were predicted and comparisons were made with CFBC, PFBC-CC, and supercritical units. Two 400 MW IGCC units were proposed to be installed. Their net efficiency is planned to be more than 43%. They are designed to gasify bituminous coals with high sulfur content (2.5 to 3%) from Yanzhou in Shangong. Sulfur will be recovered as elemental sulfur with a predicted removal efficiency of 98%. Three other gasification plants are planned to be developed by Shell in partnership with Sinopec in China, and a fourth one is under feasibility study. The plants will all produce syngas for ammonia/urea production or H_2 for other chemical plants (methanol, oxo), replacing naphta reformers, oil gasifiers, or outdated coal gasifiers.

MHI: Mitsubishi Heavy Industries (MHI) consists of an air-blown MHI gasifier that is divided into two sections: a lower combustion section, which is connected by a diffuser to an upper reducing section. Dry pulverized coal is fed at two points into the gasifier, with half of the coal being fed into the combustor together with air, where it is burned to produce CO. The temperature inside the combustor is sufficiently high to melt the coal ash without the addition of flux. The slag runs to the bottom of the gasifier, where it is quenched in a water bath and removed using a lock hopper system. The gas produced in the combustor rises to the reducing section, where the remaining coal is added. Coal is then gasified in the reducing section to produce a low CV syngas mainly formed of nitrogen. As the reducer section is at a lower temperature than the combustor section, any molten ash carried upwards is solidified. The syngas produced exits the gasifier through a syngas cooler, and then cyclones are used to collect the chars as the coal is not completely gasified in the reducing section. Chars collected in the cyclones are then reinjected at the base of the gasifier to ensure complete carbon conversion. Because of the very high temperatures reached in the combustion section, this type of gasifier is well suited to gasify the very high ash-melting point Australian coals without any addition of fluxing agent. The MHI gasification technology has been tested in Nakoso (Japan) in two pilot-scale gasifiers. A new IGCC project has been started that is a 250 MW air-blown IGCC demonstration plant located in Nakoso, where the former pilot plants were based, and will process up to 1500 ton/day of coal, which is about nine times more than the former 200 ton/day pilot plant. The system will have a unique feature: The oxidizing gas will be partially extracted from the gas turbine compressor and will be enriched with oxygen coming from an independent air separation unit, making the gasifier operation more stable and giving a certain flexibility to the system that does not exist in the two highly integrated European IGCC plants. An advantage of the MHI two-stage dry-fed entrained flow gasifier is that the syngas temperature at the outlet of the gasifier is not as high as the one flowing out of a one-stage gasifier. This means that the process does not require a large radiant cooler or a quenching system to mix cold recycled gas with the syngas. The overall cost of the process should then be less than that of existing IGCC plants. The raw gas produced together with the fly ash and the remaining char particles go up toward the exit of the gasifier. They enter a syngas cooler, where they are cooled to 450°C prior to going through a cyclone and a filter that retain most of the fly ash and the char particles, which are finally reinjected into the gasifier by pneumatic transport under nitrogen. The syngas goes successively through a water scrubber to remove halides and is desulfurized to be cleaned sufficiently to comply with the strict tolerance limits of fuel cells.

Texaco (now GE): The gasifier is a pressure vessel with a refractory lining that operates at temperatures in the range 1250 to 1450°C and pressures of 3 MPa for power generation and up to 6 to 8 MPa for H_2 and chemical synthesis. Figure 13 illustrates key features of the gasifier. The feedstocks, oxygen, and steam are introduced through burners at the top of the gasifier. Solid feedstocks such as coal are pre-processed into a slurry by fine grinding and water addition. The slurry is pumped into the burner, and the water, which is added with the slurry, replaces most of the steam that should normally be injected into the system. Raw gas and molten ash produced during coal gasification flow out toward the bottom of the gasifier. Two alternatives are then available for the recovery of the ash and for cooling the raw gas. The raw gas either can be cooled and cleaned from the slag ash by water quenching, or it can be cooled in a radiant syngas cooler from 1400 to 700°C. The heat recovered in the second option is then used to raise steam to be used in the process or for power generation. Molten slag flows down the heat-recovery steam generator and is quenched in a batch at the bottom of the cooler and finally removed through a lock hopper system. The quench alternative is the preferred option for coal feedstocks, as they could contain traces of salts (sodium and calcium) that could be corrosive for the syngas coolers at high temperatures.

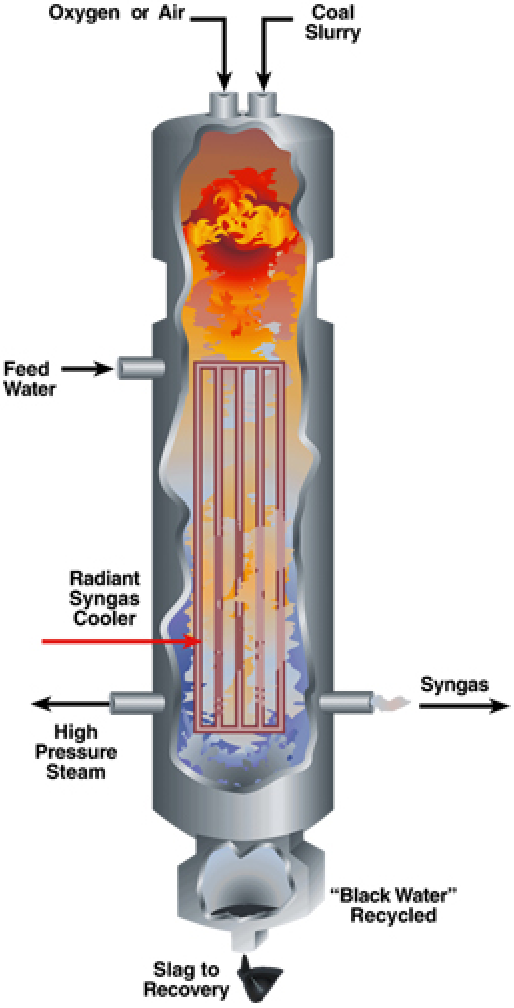


Figure 12. The Texaco Entrained Flow Gasifier [51]

However, this alternative could be a disadvantage for power generation, as thermal efficiency is slightly lowered. There are several existing projects based on Texaco technology, including an IGCC project, the Polk Power Station managed by Tampa Electric Corp. During the first three commercial years of operation, ten different coals or coal blends were tested to determine the cheaper feedstock to process while respecting new environmental regulations. The slag removal system of the Polk Power Station was designed for processing coals with a maximum of 12% (Wt dry basis) ash content. The operating temperature of the gasifiers has to be high enough for the coal mineral matter to melt and flow freely down the bottom of the gasifier. Texaco has fixed the minimum heating value of the coals at 30 MJ/kg to produce enough syngas to fully load the combustion turbine. It would be necessary to increase the oxygen supply size as well as the slurry delivery system capacity to be able to run the plant with a lower heating value coal. The plant is designed to accommodate coals with sulfur contents of up to 3.5% (Wt dry basis). Expensive modifications of the acid gas removal system were required for higher sulfur content coals than the first base coal (Pittsburgh No 8-1 with a sulfur content of around 2.5%). Following major problems, the company decided to switch to coal blends with a lower sulfur content. The limit in chlorine concentration in the coals was fixed at 0.15% (dryash). A higher concentration of chlorine in coals would damage the system. Other coal properties have an influence on the technical and economic aspects of the Texaco-based IGCC operation and necessitate coal testing in the device prior to selecting them for the Polk Power Station. The Texaco technology is also used for chemical plants. Five chemical plants were built after 1993 in the U.S. Eastman Chemicals (Kingsport, TN) owns two Texaco quench gasifiers that operate at 70 bar and 1400°C for the production of acetic acid and acetic anhydride. Although the facility is configured for the purpose of making acetyl chemicals, the company claims that gasification and cleanup plants are completely compatible with an electric power option, and in fact an electric power option of 523 MWe is reported to be under development at Kingsport. This is in line with the new projects of cogeneration of chemicals and electricity sponsored by the U.S. DOE under the Vision 21 program. Another U.S. company, Waste Management & Processors, Inc., is presently conducting a technoeconomic feasibility study in partnership with Texaco, Sasol, and Nexant for the development of one of the three demonstration Early Entrance Coproduction Plants (EECPs) under the Vision 21 program. The objective is the commercialization of a coal gasification/liquefaction technology to produce ultra-clean Fischer-Tropsch transportation fuels with power, chemicals, or steam as co-products. The proposed plant location is at the Gilberton Power Plant cogeneration facility in Gilberton, Pennsylvania. It involves the gasification of local waste coals, mainly high-ash-content anthracite wastes derived from an on-site coal cleaning operation that contains coal fines, coal dust, and dirt. Another demonstration EECP project is being developed by Texaco in collaboration with Rentech (Fischer-Tropsch Technology), Brown and Root Services, Praxair, and GE Power Systems for the production of electricity and chemicals from coal or petroleum coke. The project involves technical and economic studies of several process options, including syngas composition, Fischer-Tropsch product upgrading, wastewater treatment, catalyst/wax separation, acid gas removal, tail gas utilization, and site selection. There is also a plan for the construction by coal power of a 430 MW IGCC plant based on the Texaco technology near the Hatfield colliery in the North of England. The IGCC project with CO_2 removal and production of H_2 is being studied by Jabobs Consultancy in cooperation with GE. The IGCC power plant is configured to be capable of removing 75% of the feed carbon as CO_2 prior to combustion in the gas turbine. By performing a ‘sour shift’ of the syngas, most of the carbon monoxide should be converted into carbon dioxide and an equal volume of hydrogen. If carbon dioxide removal is performed then the fuel for the combustion turbine will consist mainly of H_2.

BBP: Babcock Borsig Power (BBP) technology, also known as the Noell entrained flow technology, was first developed in 1975 in the former East Germany for the gasification of lignite in a 3 MW pilot plant. A full-scale (130 MW) gasifier was built in the 1980s to produce syngas and town gas. The technology was known as the GSP process before being acquired by Noell in 1991. The process can be a dry-fed or a liquid-fed oxygen-blown slagging gasifier. If solid fuel is to be gasified, it is first pulverized, then pneumatically conveyed to the feeding system, and dry fed together with oxygen and steam through a burner located at the top of the gasifier. Depending on the fuel ash content, the gasification chamber can be covered by either a cooling screen or a cooling wall. Both the refractory and the solid slag provide thermal insulation and maintain the tube surface temperature below 230°C. To allow the solidified slag to regenerate continuously, only fuels with an ash content of more than 1 wt%, such as coals, can be processed in the gasifier lined with a cooling screen. Heat removed by the cooled tube wall represents 2 to 3% of the total heat produced during gasification and is used to generate low-pressure steam. Syngas saturated with water is further cooled to 150 to 200°C and recycled to the quench sprays within the gasifier. The bottom part of the gasifier consists of a quench bath that cools and solidifies the slag, which is then removed in a granular form. The only Noell gasifiers in commercial operation are at Schwarze Pumpe (Germany) and the new BASF Seal Sands located in Middlesbrough in the UK. The BBP Research and Development center based at Freiberg (Germany) comprises two facilities with capacities of 5 and 10 MW. The smaller one was originally designed in 1979 for the gasification of both solid and pulverized solid materials. The pilot plant is presently used by Dow Chemical for the development of the gasification of chlorinated wastes. The second one was also designed for the gasification of pulverized materials (coal, waste), liquids, and slurries (waste oil, sludge, paint waste) and built in 1997. A wide range of coals from anthracites to brown coals have been gasified in the two pilot plants since the 1980s. BBP claims that it is capable of providing appropriate test conditions to optimize feedstock preparation prior to gasification as well as to determine the optimum gasification conditions for more than 80 different fuels, including 30 coals.

E-Gas: The E-Gas (formerly Destec) coal gasifier is a slurry-fed, pressurized, upflow, entrained two-stage slagging gasifier. Figure 13 illustrates the key features. The dry coal concentrations in the slurry range from 50 to 70 wt%, depending on the inherent moisture and quality of the feed. Part of the coal slurry (80%) is injected with oxygen (95%) through twoburners at the lower stage of the gasifier, where it is partially combusted at a temperature of 1350 to 1400°C and a pressure of 3 MPa. Molten ash formed flows down the gasifier and is removed through a tap hole into a water quench. There is no lock hopper for ash removal, which has the advantage of reducing the overall height of the system. The fuel gas produced in the lower stage flows upwards into the upper stage, where it can react with the remaining 20% coal slurry. This two-stage process presents the advantage of producing a gas with a higher calorific value than the one produced in a one stage process. The crude gas exiting the gasifier at a temperature of around 1050°C is cooled to 370°C in a firetube syngas cooler. This unit generates saturated high-pressure steam. The firetube syngas cooler is a boiler system, with the hot gas circulating on the boiler side, as opposed to a water syngas cooler, in which water circulates in tubes in a syngas tank. The firetube is reportedly considerably cheaper than the ones used in the Shell, Texaco, and Prenflo processes. After the cooling step the syngas is cleaned with filters to remove large ash and char particles that are pneumatically reinjected into the gasifier. The filter elements, made of metal for an acceptable resistance to corrosive syngas, are periodically back pulsed with high-pressure syngas to remove particulate cake formed on their surface. The particulate cake falls to the bottom of the vessel and is pneumatically transferred together with the high-pressure syngas to the first stage of the gasifier, where it is recycled. Finally, the particulate-free syngas proceeds to the low-temperature heat recovery system, where it is scrubbed with sour water condensed from the syngas to remove troublesome chlorides and trace elements that could cause corrosion within the piping and vessels as well as form undesirable products in the acid gas removal system. After scrubbing and reheating, the syngas enters the COS hydrolysis unit, where the COS present in the syngas is converted to H_2S. The syngas is then cooled through a series of shell and tube exchangers to 35°C before entering the acid gas removal system. This cooling step also condenses water from the syngas. Most of the ammonia (NH_3) and some of the carbon dioxide (CO_2) and H_2S present in the syngas are absorbed in the water as dissolved gases. Wabash River (West Terre Haute, IN) is the only E-Gas gasifier in operation. Prior to the repowering of the Wabash River plant to an IGCC, some tests of bituminous coals, including high-sulfur coals, were performed in a 2200 ton coal/day plant based in Plaquemine, LA in the early 1990s. The Wabash River power plant is designed to use a range of local coals with a maximum sulfur content of up to 5.9% (dry basis) and a higher heating value of 31.4 MJ/kg (moisture and ash free). It is presently operating on Illinois No. 6 coal. Alternative fuels (petcoke) have also been successfully tested at Wabash River, and future tests may include coal fines. Coal fines are believed to be a promising fuel in the locality of the Wabash River facility as it is produced by the existing operations of the adjacent mine. They are also available from surface reserves, where the fines have been landfilled in the past and are predicted to be 40 to 60% cheaper than the present coal delivered to the facility.

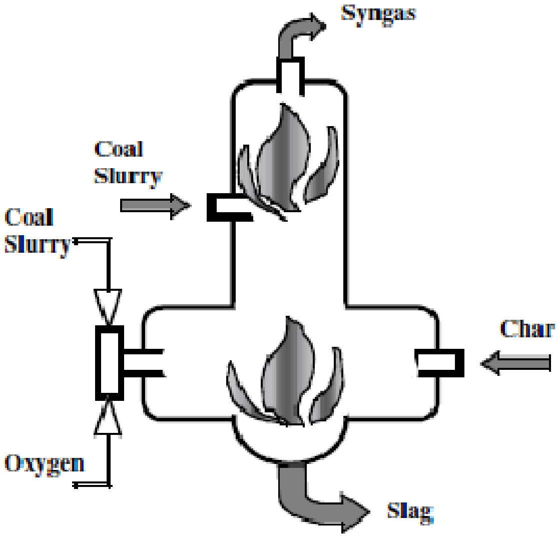


Figure 13. Key Features of the E-Gas Gasifier [10]

Prenflo: Coal is fed together with oxygen and steam through four burners located at the lower part of the gasifier. Syngas is produced at a temperature of 1600°C and is quenched at the gasifier outlet with recycled, cleaned gas to reduce its temperature to 800°C. Then the syngas flows up a central distributor pipe and down through evaporator stages before exiting the gasifier at a temperature of 380°C. The raw gas is then dedusted in two ceramic candle filters, and a part of it is recirculated into the syngas cooler. The syngas is finally washed in a Venturi scrubber. Slag formed during the gasification process is quenched in a water bath and is then removed through a lock hopper system. The only commercial-scale unit is based in Puertollano in Spain (capacity of 338 MWe). It is the largest unit worldwide based on solid fuels. The plant has been operating since 1996 and can process up to 2600 ton/day of coal/petcoke fuel mixed with limestone (2% weight) and produces 180,000 m 3 /day of raw gas. The annual production of slag (85% of the ash in weight) and fly ash (15% of the ash in weight) are 120,000 ton and 12,000 ton per year, respectively. The demonstration project has now attained commercial development with a gross efficiency of 47.2% (net efficiency of 42%).

Gas Composition (mol %)	**Coal** gasified with…			
	Oxygen			Air
	Fixed-bed Dry ash	Entrained-flow Dry feeding	Entrained-flow Slurry feeding	Fluidized bed
CO	57	65	49	22
H_2	26-30	29	34	17
CO_2	4	2	10	7
CH_4	6	0.01	0.2	0.5
N_2	2	2	1	44

Table 5. Typical compositions of gases from gasifiers* [1]

* Data from actual gasifiers. Products depend on the coal used, the oxygen purity and the reaction conditions.

2.5.2 IGCC Technical Description

IGCC power plants involve a complex chain of activities that start with a carbon-based material - in this case, coal - and result in electrical power. The coal gasification process begins with a controlled mixture of coal, oxygen, and steam in a gasifier. An air separation unit separates air into its component parts to supply the gasifier with a stream of oxygen. Using a combination of heat and high pressure, the gasifier converts the constituents of coal into "syngas". Byproducts captured in the gasifier could have commercial value, depending on local market conditions. For example, ash material produced in an IGCC plant may be used as a filler material in construction projects and building products. Alternatively, slag, which falls to the bottom of the gasifier may be used in road gravel.

The syngas is then passed through a water gas shift reactor and reacted over a catalyst with added steam to convert the majority of the CO into carbon dioxide (CO_2) and additional H_2. The syngas will also have small amounts of other impurities (e.g. hydrogen sulfide) which are removed during the gas clean-up process. Hydrogen sulfide will be separated from the syngas and converted to elemental sulfur or possibly sulfuric acid. The sulfur byproducts may also have commercial value in a variety of products (e.g. fertilizer), depending on local market opportunities. Most of the CO_2 is removed from the syngas leaving behind H_2-rich syngas.

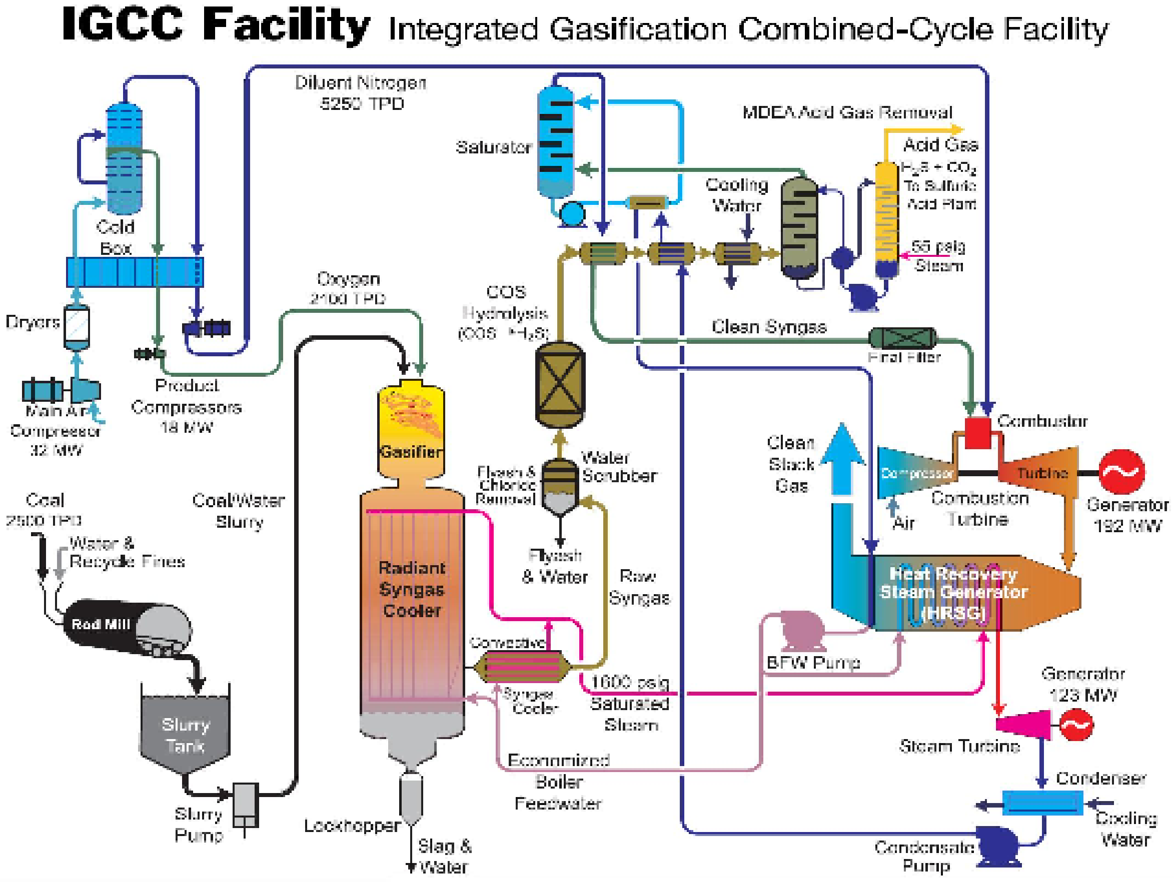


Figure 14. IGCC Facility [55]

One of the things that make IGCC plants more efficient is the combined use of a gas turbine and steam turbine to produce electricity. The hydrogen-rich syngas is first fed into a gas turbine to generate electricity. The waste heat from the gas turbine is used to power a steam turbine, which in turn creates more electricity. Finally, much of the water used in this process will be recycled in the plant while some will be evaporated in a cooling tower.

Gasification may be one of the best ways to produce clean-burning hydrogen for tomorrow's cars and power-generating fuel cells. Hydrogen and other coal gases can be used to fuel power-generating turbines, or as the chemical building blocks for a wide range of commercial products, including diesel and other transport fuels.

Reliability and availability have been challenges facing IGCC development and commercialisation. Cost has also been an issue for the wider uptake of IGCC as they have been significantly more expensive than conventional coal-fired plant.

2.5.3 An IGCC Power plant in numbers

Unit size

As gasifiers are pressure vessels, they cannot be fabricated on site in the same way that PCC boilers can. Large gasifiers are difficult to transport, simply because of their weight and sheer size, and this may prove to restrict their eventual use for sizes much above 300 MWe.

Thermal efficiency

The driving force behind the development is to achieve high thermal efficiencies together with low levels of emissions. With all power generation routes, it is important to assess and compare thermal efficiencies under normal load following conditions, and not just when the unit is operating under full load. It is hoped to reach efficiencies of over 40%, and possibly as high as 45% with IGCC. Higher efficiencies are possible when high gas inlet temperatures to the gas turbine can be achieved. At the moment, the gas cleaning stages for particulates and sulphur removal can only be carried out at relatively low temperatures, which restricts the overall efficiency obtainable.The main incentive for IGCC development has been that units may be able to achieve higher thermal efficiencies than PCC plant, and be able to match the environmental performance of gas-fired plants.

Plant Overview

This analysis is based on a 640 MWe (net power output) Integrated Gasification Combined-Cycle (IGCC) plant using radiant-only gasification technology. The radiant-only configuration consists of a radiant synthesis gas cooler followed by a water quench. Two pressurized, slurry-fed, entrained flow gasification trains feed two advanced F-Class combustion turbines. Two heat recovery steam generators (HRSGs) and one steam turbine provide additional power.

Operation

The plant uses an improved version of the gasification technology which is currently in operation at the 250 MWe Tampa Electric IGCC plant in Polk County, FL. All technology selected for the plant design is assumed to be available to facilitate a 2010 startup date for a newly constructed plant. Two gasification trains process a total of 6,005 tons of coal per day. A slurry (63 percent by weight coal) is transferred from the slurry storage tank to the gasifier with a high-pressure pump. Oxygen (O_2) is produced in a cryogenic air separation unit. The coal slurry and O_2 react in the gasifier at about 5.6 MPa at a high temperature (in excess of 1,316°C) to produce syngas. Hot syngas and molten solids from the reactor flow downward into a radiant heat exchanger, where the syngas is cooled to 593°C and the ash solidifies. Raw syngas continues downward into a quench system where most of the particulate matter (PM) is removed and then into the syngas scrubber where most of the remaining entrained solids are removed along with halogens and ammonia. Slag captured by the quench system is recovered in a slag recovery unit. The gas goes through a series of additional gas coolers and cleanup processes, including a carbon bed for mercury (Hg) removal. To capture CO_2, a WGS reactor containing a series of two shifts with intercooled stages converts a nominal 96 percent of the carbon monoxide to CO_2. Carbon dioxide is removed from the cool, particulate-free gas stream with Selexol solvent. The dual-absorber Selexol acid gas removal (AGR) process preferentially removes hydrogen sulfide (H_2S) as a product stream, leaving CO_2 as a separate product stream. The CO_2 is dried and compressed to 15.3 MPa for subsequent pipeline transport. The compressed CO_2 is transported via pipeline to a geologic sequestration field for injection into a saline aquifer, which is located within 50 miles of the plant. A Brayton cycle, fueled by the syngas, is used in conjunction with a conventional subcritical steam Rankine cycle for combined-cycle power generation. The limiting factor that determines the use of a subcritical steam cycle is the maximum design pressure of 12.4 MPa, which can be tolerated in the radiant cooler. The two cycles are integrated by generation of steam in the HRSGs, by feedwater heating in the HRSGs, and by heat recovery from the IGCC process (radiant syngas cooler). The HRSG/steam turbine cycle is 12.4 MPa/538°C/538°C. The plant produces a net output of 555.7 MWe. This configuration results in a net plant efficiency of 38.2 percent (HHV basis), or a net plant HHV heat rate of 9424 KJ/KWh.

Environmental Performance

The environmental specifications for a greenfield IGCC plant are based on the Electric Power Research Institute CoalFleet User Design Basis for Coal-Based IGCC Plants specification. Low sulfur dioxide (SO_2) emissions (less than 4 ppmv in the flue gas) are achieved by capture of the sulfur in the Selexol AGR process, which removes over 99 percent of the sulfur in the fuel gas. The resulting hydrogen sulfide-rich regeneration gas from the AGR system is fed to a Claus plant, producing elemental sulfur. Nitrogen oxides emissions are limited by nitrogen dilution in the gas turbine combustor to 15 ppmvd (as nitrogen oxide at 15 percent O_2). Filterable PM discharge to the atmosphere is limited by the use of the syngas quench in addition to the syngas scrubber and the gas washing effect of the AGR absorber. Ninety-five percent of the Hg is captured from the syngas by an activated carbon bed.

2.5.4 Commercial-scale IGCC Powerplants

A number of demonstration units, mainly around 250 MWe size are being operated in Europe and the USA. All the current coal-fueled demonstration plants are subsidised. The European plants are part of the Thermie programme, and in the US, the DOE is part funding the design and construction, as well as the operating costs for the first few years. Some are repowering projects, but from the point of view of demonstrating the viability of various systems, they are effectively new plant, even though tied to an existing steam turbine.

There are currently four commercial-scale, coal-based IGCC demonstration plants worldwide and a number of other IGCC projects have been proposed. IGCC plants also operate at Schwarze Pumpe in Germany and Vresova in the Czech Republic.

Location	Fuel	Power Output	Commenced Operation
Buggenum, Netherlands	Coal/Biomass	250MW	1994
Polk, USA	Coal/Petcoke	250MW	1996
Puertollano, Spain	Coal/Petcoke	335MW	1997
Wabash, USA	Coal/Petcoke	260MW	1995

Table 6. Commercial-scale, Coal-based IGCC Demonstration Plants in Operation [36]

- The Wabash River CCT project successfully demonstrated commercial application of the coal gasification technology in conjunction with electric power generation. Operating time exceeded 15,000 hours, with over 1.5 million tons of coal processed and about 4 million MWh of power produced. The combustion turbine generated 192 MWe and the repowered steam turbine generated 104 MWe. With the system's parasitic load of 34 MWe, net power production was 262 MWe, which met the target goal. Carbon conversion exceeded 95%. The plant operated successfully on baseload dispatch in the power grid, and continues to operate as a privately owned facility providing power.
- A state-of-the-art integrated coal gasification combined-cycle (IGCC) power plant, Tampa Electric's Polk Power Station produces enough electricity to serve 75,000 homes. Polk Unit One is located on unmined land surrounded by former phosphate mining land to the east, and a berm developed as a cooling reservoir to the south. The design of the maximized plant water recycling and re-use, and minimized groundwater withdrawal and offsite discharges. The 250-megawatt IGCC facility began commercial operation in the fall of 1996. Construction on Polk Unit Two began in 1998 and Unit Three in 1999. These two 180-megawatt simple cycle combustion turbines use natural gas and distillate oil to generate electricity. Unit Two and Unit Three started commercial operation in July 2000 and May 2002 respectively. Polk Units four and five, two 160-megawatt (MW) units were completed in April 2007. The two new simple-cycle peaking units use natural gas to generate electricity.
- The Puertollano IGCC project has been driven by the demand of energy efficient, environmentally friendly and cost effective coal generation technologies. The 335 MWe (ISO) demonstration plant has been designed to use a 50/50 mixture of high ash local coal and petroleum coke from a nearby refinery. The project was selected as Target Project by the European Commission and awarded funding by the THERMIE program focused on the need to take short-term actions to assure reliable clean coal technology for the future power generation. The plant design innovative features focused on two main targets: im-

proved efficiency (45% net, ISO conditions) and reduced emissions. The design concept is arranged at the maximum integration level (air and nitrogen streams) and large capacity components (2600 t/day gasifier and 200 MW gas turbine) were selected.

- Another IGCC success story has been the 250 MW Buggenum plant in The Netherlands. It has good availability. This coal-based IGCC plant currently uses about 30% biomass as a supplemental feedstock. The owner, NUON, is paid an incentive fee by the government to use the biomass. NUON is constructing a 1300 MW IGCC plant in the Netherlands. The Nuon Magnum IGCC power plant will be commissioned in 2011. Mitsubishi Heavy Industrie has been awarded to construct the power plant.

3 Numerical Simulation of Coal Gasification

3.1 Literature and Research

There has been a lot of research in the area of gasification not only because of the fact that gasification as a process of utilizing the coal is used for over a century now, but also because of the large number of reactions that involves. However, despite the vast quantity of literature concerning gasification, only a small part of it is relevant to entrained flow gasifiers and gasification at high temperatures and pressures. The relevant literature is presented on the next table.

	Pressure (bar)	Temperature - max (K)	Gasifying mean	Gasifier characteristics
Wen, Chaung [1979]	24	~ 2400	Oxygen / Steam	Texaco Gasifier ~ 10 t/d
Govind, Shah [1984]	24.31 21.28	2370	Oxygen / Steam	Texaco Gasifier ~ 10 t/d
Vamvuka et. al. [1995]	1 and 20	2000	Oxygen / Steam	50 g / s
Ni, Williams [1995]	10 - 38	1800	Oxygen	Shell coal gasifier
Chen et. al. [2000]	27	1897	Air	200 t/d two-stage Gasifier
Liu et. al. [2000]	1 - 24	~ 1600	Oxygen / Steam	60 – 132 g / s
Choi et. al. [2001]	Up to 24.51	1500	Oxygen	1 t/d KIER Gasifier
Park et. al. [2001]	1	1800	Oxygen	0.5 t / d
Wall et. al. [2002]	Effects of Pressure in coal combustion and Gasification			
Watanabe, Otaka [2006]	20	2300	Air	CRIEPI 2 t / d Gasifier

Table 7. Entrained Flow Coal Gasification Literature

Wen and Chaung [26] and *Govind and Shah* [27] proposed mathematical models to simulate the Texaco down-flow entrained-bed pilot-plant gasifier using coal liquefaction residues and coal-water slurries as feedstocks. These models describe the physical and chemical processes occurring in an entrained coal gasifier. The gasification kinetics describes different complex reactions occurring in the gasifier and the hydrodynamics describes mass, momentum and energy balances for solid and gas phases. Temperature, concentration and velocity profiles along the reactor height were obtained by solving the mass, momentum and energy balances. Parameter studies were made to provide a better understanding of the reactor performance for various inlet feed conditions. One of the conclusions of the above publications is that the gas composition leaving the gasifier and the final carbon conversion depends on three essential parameters: the fuel rate, the oxygen to fuel ratio, and the steam-fuel ratio.

A one-dimensional, steady-state model for an entrained flow coal gasifier is developed by *Vamvuka et. al.* [32] incorporating thermo gravimetric analysis data on a bituminous coal. The model is based on mass and energy balances, heterogeneous reaction rates and homogeneous gas-phase equilibria. The resulting set of non-linear mixed ordinary differential-implicit algebraic equations was solved by a modified Euler method in conjunction with a non-linear algebraic equation solver. Temperature, reaction rate and composition profiles in a tubular gasifier were predicted at 0.1 and 2 MPa operating pressures, at constant feed rates. The calorific value of the gas produced was higher at 2 MPa.

Ni and Williams [31] perform a simulation method for an entrained-flow coal gasifier on the basis of equilibrium, mass and energy balances. The Shell coal gasifier was studied as a typical model for an entrained-flow gasifier using dry pulverized coal in an oxygen-blown reactor. The effects of the coal-oxygen-steam ratios, the temperature and the pressure on the gasified products and steam production were studied. Some of the conclusions are: For an entrained-flow coal gasifier working under these conditions the oxygen to coal ratio is the most important control variable for the gasifier operation in all cases. The gasifier exit temperature is an important control variable in gasifier performance. The steam to coal ratio influences the molar fraction of gaseous products very much, but at different values of oxygen to coal ratio. Pressure has almost no effect on the gasifier performance in the region studied.

A comprehensive three-dimensional simulation model was developed for entrained flow coal gasifiers by *Chen et. al.* [13]*.* In the model, the numerical methods and the sub models conventionally used for the pulverized coal combustion modeling were used. An extended coal gas mixture fraction model was applied to simulate the gasification reaction and reactant mixing process. The influence of turbulence on the gas properties was taken into account. A series of numerical simulations were performed for a 200 t/d two-stage air blown entrained flow gasifier recently developed for the IGCC process. The predicted gas temperature profile and the exit gas composition were in general agreement with the measurements. Model simulations illustrating the importance of accounting for varying coal off-gas and the effects of turbulence/reaction affecting the prediction capability were also presented.

A model for a pressurized entrained flow coal gasifier is presented by *Liu et. al.* [34] with the effect of pressure, reaction kinetics and char structure on the gasification reactions being outlined. A sensitivity analysis to reaction kinetics and char structure was performed, and model predictions are compared with published atmospheric and high-pressure gasification data. It was found that both reaction kinetics and char structure are important in predicting coal gasification. The initial surface area may be more significant than intrinsic reactivity for bituminous coal chars. Low-pressure gasification kinetics (i.e. pressure order) cannot be extrapolated to high-pressure conditions. A significant difference in predicted carbon conversion was observed between various char structural models. It is suggested that the random pore model gives a reasonable prediction. Volatile matter has significant effect on carbon conversion due to the formation of high-surface area char particles. Comparisons with previous models and sensitivity analyses suggest that it is necessary to include the effect of char structure, and more sophisticated reaction kinetics than single order rates are required when modeling coal gasification.

The coal gasification process of a slurry feed type, entrained-flow coal gasifier is numerically predicted in the paper of *Choi et. al.* [15]. By dividing the complicated coal gasification process into several simplified stages such as slurry evaporation, coal devolatilization and two-phase reactions coupled with turbulent flow and two-phase heat transfer, a comprehensive numerical model was constructed to simulate the coal gasification process. The k–ε turbulence model was used for the gas phase flow while the Random-Trajectory model was applied to describe the behavior of the coal slurry particles. The unreacted-core shrinking model and modified Eddy break-up (EBU) model, were used to simulate the heterogeneous and homogeneous reactions, respectively. The simulation results obtained the detailed information about the flow field, temperature and species concentration distributions inside the gasifier. Meanwhile, the simulation results were compared with the experimental data as a function of O_2/coal ratio. It illustrated that the calculated carbon conversions agreed with the measured ones and that the measured quality of the syngas was better than the calculated one when the O_2/coal ratio increases. This result was related with the total heat loss through the gasifier and uncertain kinetics for the heterogeneous reactions.

Coal gasification processes in a slurry-feed-type entrained-flow gasifier are studied by *Park et. al.* [29]. Novel simulation methods as well as numerical results are presented.. Very detailed results regarding the impact of the O2/coal ratio on the distribution of velocity, temperature and concentration are obtained. Simulation results show that the methods are feasible and can be used to study a two-phase reacting flow efficiently.

In the paper of *Wall et. al.*[35], the pressure effect on a variety of aspects of coal reactions reported in the open literature has been reviewed. The pressure has been found to significantly influence the volatiles yield and coal swelling during devolatilization, hence the structure and morphology of the char generated. More char particles of high porosity are formed at higher pressures. Char structure appears to play a significant role in burnout of residual char and ash formation. In general, at higher pressures, coal particles burn quicker and form finer ash particles. Increasing reactant pressure enhances char combustion and gasification reaction rate, which can be understood by an adsorption–desorption mechanism. These factors have been applied to the understanding of a practical high-pressure gasifier.

The paper of *Watanabe and Otaka* [24] presents modeling of a coal gasification reaction, and prediction of gasification performance for an entrained flow coal gasifier. The purposes of this study are to develop an evaluation technique for design and performance optimization of coal gasifiers using a numerical simulation technique, and to confirm the validity of the model. The coal gasification model suggested in this paper is composed of a pyrolysis model, char gasification model, and gas phase reaction model. A numerical simulation with the coal gasification model is performed on the CRIEPI 2 tons/day (T/D) research scale coal gasifier. Influence of the air ratio on gasification performance, such as a per pass carbon conversion efficiency, amount of product char, a heating value of the product gas, and cold gas efficiency is presented with regard to the 2 T/D gasifier. Gas temperature distribution and product gas composition are also presented.

3.2 The “HotVeGas” Project

High requirements rise for future coal-fired power stations, regarding resources sufficiency, environment-friendliness, reliability and economy. The immense growth rates of the energy consumption make clear that limiting on a long-term basis the output of the CO_2-Emissions cannot be achieved alone by more efficient power station technologies. Fossil sources of energy can only in co-operation with CO_2 - Capture technologies, guarantee successful CO_2 - Emissions decrease.

Coal-fired power stations facilitating IGCC technology (Integrated Gasification Combined Cycle) offer the advantage of a high efficiency (>50%) and the possibility of an effective CO_2-Capture. Compared with the competitive systems, IGCC technology with CO_2-Capture exhibits clear advantages:

- Highest efficiency and/or. smallest efficiency loss
- highest fuel flexibility
- lowest emissions
- retrofitting possibility of CO_2-Capture
- operation without separation possible

A further, substantial advantage of the IGCC technology is the fact that apart from electricity, also synthetic fuels such as hydrogen, methane, methanol or liquid fuels can be produced.

Currently operating IGCC power stations achieve electrical efficiencies of approx. 45 %. Today, state of the art IGCC power stations without CO_2-Capture can be planned with an electrical efficiency of approx. 50% and can be realized in approx. 8 years.

IGCC power plants with CO_2 – capture can reach comparatively high efficiencies (> 40%). State of the art gas-cleanup, involves particle separation, water cooling, COS hydrolysis and wet desulphurization, in order to produce a suitable for gas-turbines fuel. Gas cleanup procedures for hot gaseous fuels are not established or only partly established yet. With the help of a CO SHIFT and CO_2-Seperation in a physical solvent, the gaseous fuel can be additionally released from CO_2 before entering the gas turbine.

A further considerable increase of the efficiency is to be expected with hydrogen membranes. Due to the fact that gaseous fuel after the CO_2-Capture exhibits a high H_2-concentration (>>80% H_2), the SHIFT reaction requires a strongly over-stoichiometric ratio from water vapor to CO and thus a substantial need of medium pressure steam, which must be uncoupled from the process and thus become unavailable for power generation. With employment of H_2-Membranes only a stoichiometric ratio of water vapor would be necessary to CO. Thus on one hand the need of water vapor could be strongly lowered and on the other hand the cooling on the low temperatures thermodynamically necessary for the SHIFT reaction could be avoided and thus a hotter gas for the burner of the gas turbine to be available.

The long-term development target for the CO_2-free, maximum-efficiency IGCC is therefore a high pressure high temperature gasifier with integrated hot gas cleaning at highest temperatures, H_2-Seperation by means of catalytic high temperature membranes at as high a temperatures as possible and H_2-Gasturbine with hot gaseous fuel supply.

Even if gasification is a very old technology, the knowledge about the conditions of the gasification is clearly smaller than this of combustion processes or in particular the gas combustion. In order to initiate a long-term potential from IGCC power stations, a much better knowledge of the conditions of gasification and the gas clean-up is unavoidable.

Under these circumstances, the Technical University of Munich has been assigned with the “HotVeGas” Project. The project involves a basic research for the development of future high-temperature gasification and gas-cleaning processes for IGCC-Power plant with CO_2 Capture and for the production of synthetic fuel.

The most important goal of this research is to place the necessary bases for the development of high-efficiency / high-temperature gasification processes with integrated hot gas cleaning and optional CO2-Capture for IGCC power stations and processes to the production of synthetic fuels. The project is planned having a duration of ten years and is divided in phases.

The duration of the first phase amounts to four years and the next phases are to last three years each. Emphasis for the first phase must be given to the following:

- Investigation of the gasification reactions under industrially relevant conditions at experimental-devises.
- Experimental investigations of ash and char behavior
- Creation of a data base for the modeling of thermo-chemical and thermophysical characteristics of ashes and chars under strictly reducing atmosphere
- Development of CFD models to simulate the flow, reactions and heat transfer of entrained flow gasification processes
- Research on ash reactions at high temperatures and cooling as well as high-temperature gas cleaning.

As far as the research at the field of gasification is concerned, the knowledge of high temperature reactions of the fuel, the minerals and the trace components in particular under reducing conditions exhibits a clearly smaller level of development compared with oxidizing conditions.

Experimental research on high temperature gasification of an entrained flow gasifier at temperatures up to 1800 °C and pressures up to 50 bar and the following cooling is desirable.

The modeling of reactive multi-phase flows in pressurized gasifiers places due to the multiplicity of the sub processes with parallel and sequentially occurring chemical and physical reactions a great challenge for the concept and the numeric control. The modeling of the entrained flow gasification of solid fuels exhibits a much smaller level of development in relation to the combustion of solid fuels.

The subject of this Diploma-thesis is to contribute to the above mentioned project by developing a CFD model to simulate coal gasification process in an entrained flow gasifier at high-temperature, high-pressure conditions.

3.3 The Physical Model Simulated

3.3.1 The gasifier

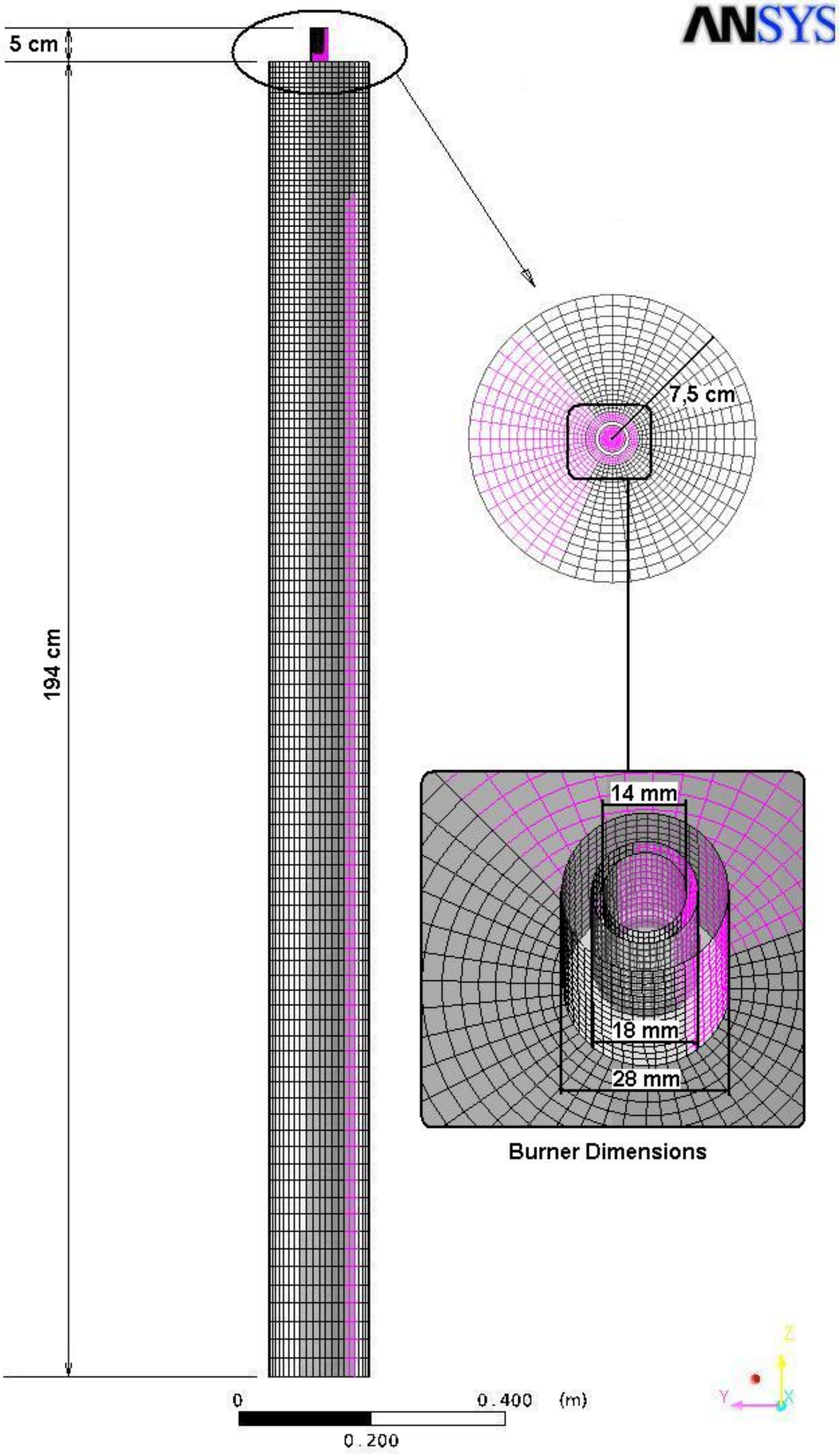


Figure 15. Gasifier Dimensions

The reactor is an entrained-flow gasifier of cylindrical shape. The gasifier geometry is represented in the CFX program through a 178844 node and 173427 hexahedric element mesh. Its capacity is 0.0337001 m³ - its height is 1.94 m and the inner diameter 0.15 m. On the upper part of the gasifier, the entrance point of coal and oxidation mean is located. The fuel in the form of grains and the oxidant in a gas phase, enter the gasifier from two different areas of a small cylindrical formation called the burner. On the top of the burner, homocentric circles divide the area in two, creating a hole in a shape of a cyclic disk with a surface of 1.535 E-04 through which the fuel enters and a cyclic ring with a surface of 3.603 E-04 through which the oxidant enters. The main body of the gasifier is a cylinder with no inner formation. The complete gasifier dimensions are shown on the figure of the previous page.

3.3.2 The coal used

For the simulations, the use of a ‘’ high volatile B bituminous coal ‘’ was assumed with a calorific value of 32,19 MJ / Kg. The coal is fed dry to the gasifier in grains of 200 μm mean diameter. The proximate and ultimate analysis of the coal used is recorded to the table that follows.

Proximate Analysis: As received		**Ultimate analysis: As received**	
Ash Fraction	0.024	Carbon Fraction	0.740
Fixed Carbon Fraction	0.581	Hydrogen Fraction	0.053
Moisture Fraction	0.043	Oxygen Fraction	0.120
Volatiles Fraction	0.352	Nitrogen Fraction	0.016
		Sulphur Fraction	0.004
		Moisture and Ash Fraction	0.067
Total	1.000		1.000

Table 8. Proximate and Ultimate coal analysis

3.3.3 The chemical reactions and reaction rates

Inside the gasifier the pressure has a fixed value and the temperature changes according to the chemical reactions that take place and whether they consume or produce energy.

As soon as the coal grains enter the main body of the gasifier, due to the high temperature, the pyrolysis phase begins and the coal particles crack into char and volatile matter. The char that is produced reacts during a gasification phase with oxygen, carbon dioxide and water. Finally, homogeneous gas phase reactions take place inside the gasifier.

Although a gasification model has already been described at the previous pages, intentionally not all the reactions mentioned are included in the numerical simulation. The reason is that some of the reactions take place in a much slower rate than others and therefore their absence does not affect the model. On the contrary, the less the reactions the less CPU time needed for a simulation to converge successfully. The chemical reactions that were finally included are:

- **Pyrolysis and devolatilization:**

  Coal → $CH_4 + CO_2 + H_2O$ + Char…………………………………… (R 3.1)

- **Char Gasification:**

  $3\,C + 2\,O_2 \rightarrow 2CO + CO_2$ …………………………………………… (R 3.2)

  $C + CO_2 \rightarrow 2CO$…………………………………………………………(R 3.3)

  $C + H_2O \rightarrow CO + H_2$ ……………………………………………………(R 3.4)

- **Gas Phase Reactions:**

  Methane Oxidation: $CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2\,H_2$ ……..(R 3.5)

  Hydrogen Oxidation: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ ………………(R 3.6)

  Carbon Monoxide Oxidation: $CO + \frac{1}{2} O_2 \rightarrow CO_2$ ……………. (R 3.7)

  Methane Reforming: $CH_4 + H_2O \leftrightarrow CO + 3\,H_2$ ……(R 3.8)

  Water Gas Shift Reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$ ………(R 3.9)

The reaction rates of each of the reactions above are presented in the table below:

Reaction Number	Reaction Rate Constants			Reference
	A	n	E (J/kmol)	
R 3.1	1.36E+06	0.68	1.30E+08	[3]
R 3.2	8710	0	17967	[4]
R 3.3	8710	0	17967	[4]
R 3.4	8710	0	17967	[4]
R 3.5	3.0E+08	-1	1.26E+08	[3]
R 3.6	6.8E+15	0	1.68E+08	[3]
R 3.7	2.2E+12	0	1.67E+08	[3]
R 3.8	4.4E+11	0	1.68E+08	[3]
R 3.9 forward	2.75E+10	0	8.38E+07	[3]
R 3.9 backward	2.65E-02	0	3.96E+03	[3]

Table 9. Chemical Reaction Rates

An Arrhenius type reaction rate is assumed for all the above chemical reactions. The form of this type of reaction rate is e.g. for reaction R 3.1:

$K\ 3.1 = A \cdot T^n \cdot e^{(-\frac{E}{RT})}$,

where A is the pre-exponential factor, T is the temperature, E is the activation energy and R is the gas constant. It has to be noted here, that the reaction rates, as mentioned before, greatly depend on coal type, gasifying agent and gasification conditions. However, no adequate data were found for high pressure gasification and hence, the applicability of the data used, to the reactions in the operating range of the entrained gasifier studied here is not verified.

As far as the devolatilization reaction is concerned, there is no standard chemical stoichiometric equation to describe the composition of volatile matter that pyrolysis produces. For the sake of simplification, it is assumed that the main volatile is the methane and also H_2O and carbon dioxide are produced with coefficients proportional to the concentration of each component in the fuel.

3.3.4 Gasification conditions

The gasification pressure inside the gasifier is set to a fixed value (2, 25 and 50 bar for each “run” respectively) and remains unchanged (except from a minor pressure drop) throughout the length of the gasifier. The gasification temperature is set to 1600 ºC but its value varies from one area of the gasifier to another depending on which are the dominant chemical reactions i.e. near the entrance point of the fuel, the temperature is lower than it is in the middle of the gasifier where the fast oxidation reactions are more intense than they are near the entrance.

The fuel grains – coal particles of a 200 μm mean diameter – and the oxidation mean – a Nitrogen/Oxygen gas mixture with a 98% N_2 , 2% O_2 mass concentration – enter the gasifier in a co-current flow from the upper side where the burner is located and they start reacting with each other as soon as they enter the gasifiers main body.

Great caution must be given to the boundary conditions. We take as given that the fuel mass flow rate available for gasification is 1 g/s. It is very important that the amount of oxidant entering the gasifier is carefully adjusted, otherwise the coal will be burned resulting into having carbon dioxide and H_2O as main products. A constant Oxygen / Fuel ratio of 0.8 is assumed for all the pressure values (5, 25 and 50 bar). This value is then set to 0.9 and 1.0 with a constant pressure of 50 bar, so that also the effect of Oxygen / Fuel ratio can be studied.

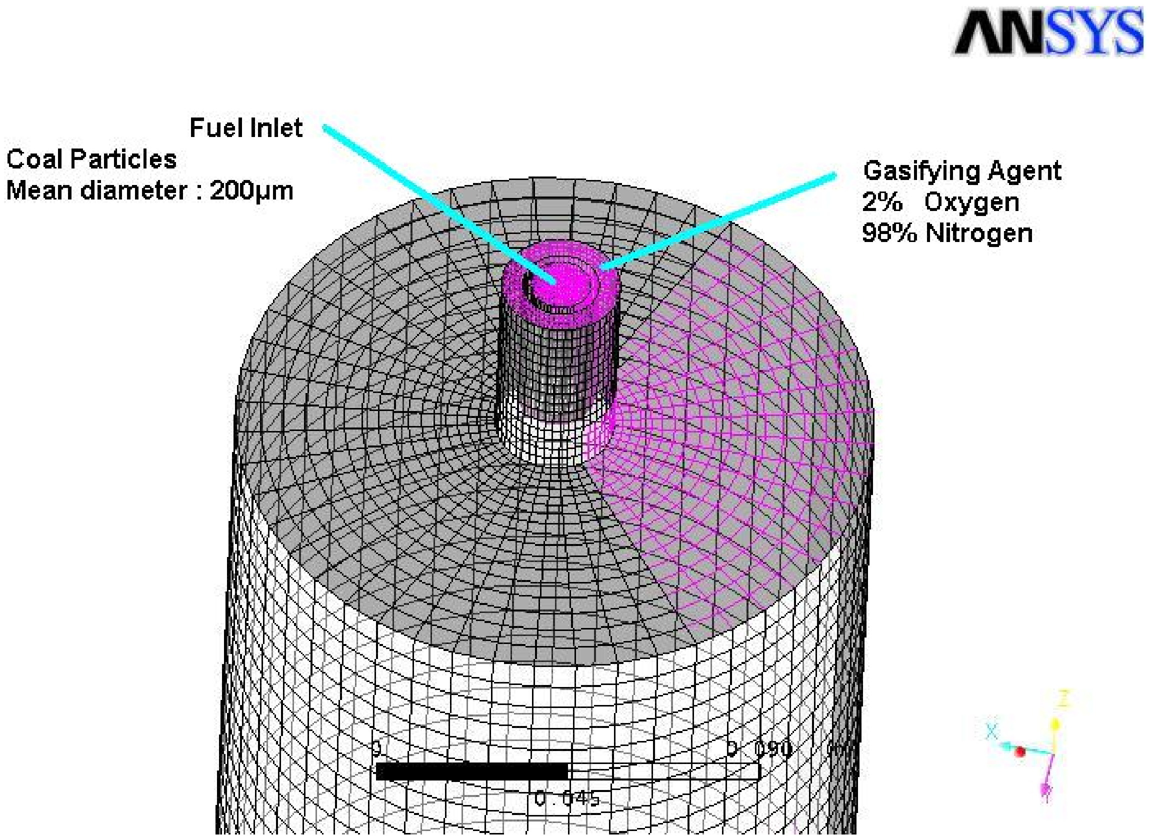


Figure 16. Flow Input

3.4 Numerical Simulation – The CFX Program

The set of equations which describe the processes of momentum, heat and mass transfer are known as the Navier-Stokes equations. These partial differential equations were derived in the early nineteenth century and have no known general analytical solution but can be discretized and solved numerically.

Equations describing other processes, such as combustion, can also be solved in conjunction with the Navier-Stokes equations. Often, an approximating model is used to derive these additional equations, turbulence models being a particularly important example. There are a number of different solution methods which are used in CFD codes.

The most common and the one on which ANSYS CFX is based, is known as the finite volume technique. In this technique, the region of interest is divided into small sub-regions, called control volumes. The equations are discretized and solved iteratively for each control volume. As a result, an approximation of the value of each variable at specific points throughout the domain can be obtained. In this way, one derives a full picture of the behavior of the flow.

More about CFX

ANSYS CFX is a general purpose Computational Fluid Dynamics (CFD) software suite that combines an advanced solver with powerful pre- and post-processing capabilities. ANSYS CFX is capable of modeling:

- Steady-state and transient flows
- Laminar and turbulent flows
- Subsonic, transonic and supersonic flows
- Heat transfer and thermal radiation
- Buoyancy
- Non-Newtonian flows
- Transport of non-reacting scalar components
- Multiphase flows
- Combustion
- Flows in multiple frames of reference
- Particle tracking

One of the most important features of ANSYS CFX is its use of a coupled solver, in which all the hydrodynamic equations are solved as a single system. The coupled solver is faster than the traditional segregated solver and fewer iterations are required to obtain a converged flow solution. Segregated solvers employ a solution strategy where the momentum equations are first solved, using a guessed pressure, and an equation for a pressure correction is obtained. Because of the 'guess-and-correct' nature of the linear system, a large number of iterations are typically required in addition to the need for judiciously selecting relaxation parameters for the variables.

ANSYS CFX uses a coupled solver, which solves the hydrodynamic equations (for u, v, w, p) as a single system. This solution approach uses a fully implicit discretization of the equations at any given timestep. For steady state problems, the timestep behaves like an 'acceleration parameter', to guide the approximate solutions in a physically based manner to a steady-state solution. This reduces the number of iterations required for convergence to a steady state, or to calculate the solution for each timestep in a time dependent analysis.

3.4.1 Options and Settings

In this paragraph, some of the most basic options and setting used in the CFX program are presented and described below:

- Simulation settings

Setting	**Option**	**Description**
Simulation Type	Steady State	

Table 10.Simulation Settings and Options

Default Domain

In the default domain of the gasifier grid the reference pressure of 5, 25 and 50 bar is applied. The domain is considered stationary and the flow non-buoyant. To simulate turbulence, the k - epsilon model is adopted while Heat transfer is modeled via the Total Energy model. Particle Tracking is activated for the monitoring of the coal grains whose mean diameter is set to 200 μm. The existence of a gas mixture containing methane, carbon dioxide, carbon monoxide, water, hydrogen, oxygen and nitrogen is assumed inside the domain. All gases obey to the transport equations except for the nitrogen which is under constrain.

Boundary Conditions

Boundary condition	Setting	Option	Description or Value
Inlet: Fuel / Gas Mixture	Flow Regime	Sub-sonic	
	Mass and Momentum	Mass Flow Rate	[10 g/s]
	Turbulence	Medium	
	Heat Transfer	Static Temperature	[300º C]
	Component Details	O_2 Mass Fraction: 0.02	
Inlet: Fuel / Particle behavior	Mass and Momentum	Zero Slip Velocity	[1 g/s]
	Particle Position	Uniform Injection	
	Particle Mass Flow	1 g / s	
	Heat Transfer	Static Temperature	[300º C]

Table 11.Simulation Settings and Options

Boundary condition	Setting	Option	Description or Value
Inlet:Oxygen	Flow Regime	Sub-sonic	
	Mass and Momentum	Mass Flow Rate	[30 g/s]
	Turbulence	Medium	
	Heat Transfer	Static Temperature	[300º C]
	Component Details	O_2 Mass Fraction: 0.02	

Outlet	Flow Regime	Sub-sonic	
	Mass and Momentum	Average static Pressure	[0 Pa relative Pressure]
Wall	Influence On Flow	No-Slip Wall	
	Heat Transfer	Temperature	[1600ºC]

Table 12.Simulation Settings and Options

Initialization

Setting	Option	Description
Velocity (Cartesian)	Z axis: - 3 m/s	
Static Pressure	Automatic with Value (A.w.V.)	[Relative Pressure: 0 bar]
Temperature	(A.w.V.)	1200º C
Turbulence Kinetic Energy	Automatic	
Turbulence Eddy Dissipation (Checked)	Automatic	
Component Details	(A.w.V.)	An initial amount of each gas is needed so that the chemical reactions start. Mass Fractions for every gas set from 0.1 to 0.2.

Table 13.Simulation Settings and Options

- Solver Control

Basic Settings	Setting	Option	Description
	Advection Scheme	High Resolution	More accurate
	Timescale Control	Auto Timescale	
	Length Scale Options	Conservative	
	Timescale Factor	0.5	
	Residual Target	1E-05 (RMS)	Convergence Criteria

Table 14.Simulation Settings and Option

3.4.2 Convergence

In the ANSYS CFX-Solver, the Navier-Stokes equations are discretized over the mesh elements to produce a set of non-linear equations for each variable at each mesh node. These equations are solved using a coupled solver. Steady state simulations – as happened in this case – are performed as a series of pseudo-timesteps. The timestep sizes are determined by the timestep setting in the Solver Control.

Equation Residual

ANSYS CFX-Solver calculates the solution to various equations given the appropriate boundary conditions and models for your particular CFD problem. At any stage of a calculation, each equation will not be satisfied exactly, and the “residual” of an equation identifies by how much the left-hand-side of the equation differs from the right-hand-side at any point in space. If the solution is “exact” then the residuals is zero. Exact means, that each of the relevant finite volume equations is satisfied precisely. However, since these equations only model the physics approximately, a converging solution does not mean that the solution exactly matches what happens in reality. If a solution is converging, residuals should decrease with successive timesteps.

Convergence Results and RMS

A measure of how well the solution is converged can be obtained by plotting the residuals for each equation at the end of each timestep. A reasonably converged solution requires a maximum residual level no higher than 5.0E-4. Typically, the RMS residual will be an order of magnitude lower than this. The RMS (Root Mean Square) residual is obtained by taking all of the residuals throughout the domain, squaring them, taking the mean, and then taking the square root of the mean. This should present an idea of a typical magnitude of the residuals.

During the solution process, using of the CFX – solver makes the monitoring of the simulation converge possible. As soon as all the equations reach the convergence target – set to 1E-05 – the solver stops so that the results can be processed.

Timestep

The value of the timestep is a very important factor as far as convergence is concerned. A large timestep can lead to a faster convergence but, if too large it can lead to the solution deviating. A typical magnitude of timestep in the modeling of coal gasification that can surely lead to convergence is 1E-03 sec and maybe even 1E-02. Greater values can be applied as timesteps if the solution has already begin to converge so that the convergence becomes faster.

The following plots depict the behavior of some of the residual equations depending on the value of the timestep. The output file of this solution process gave the results that are presented in the corresponding chapter.

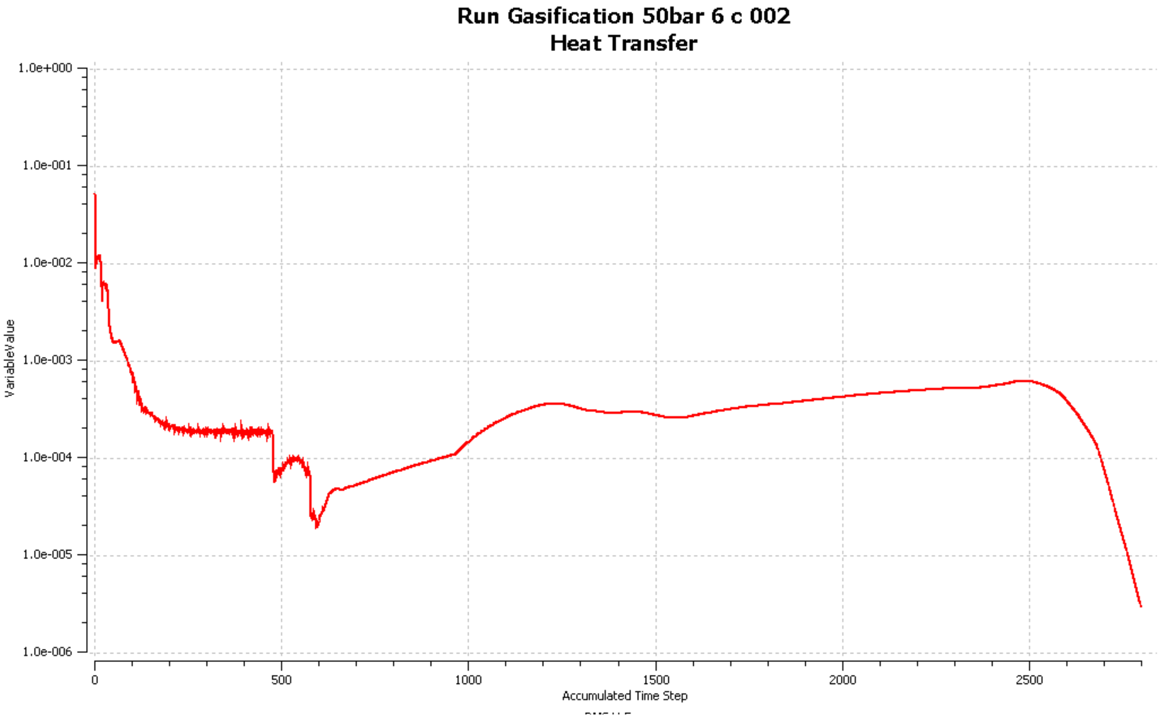


Figure 17. Residual of the solution of heat transfer equation

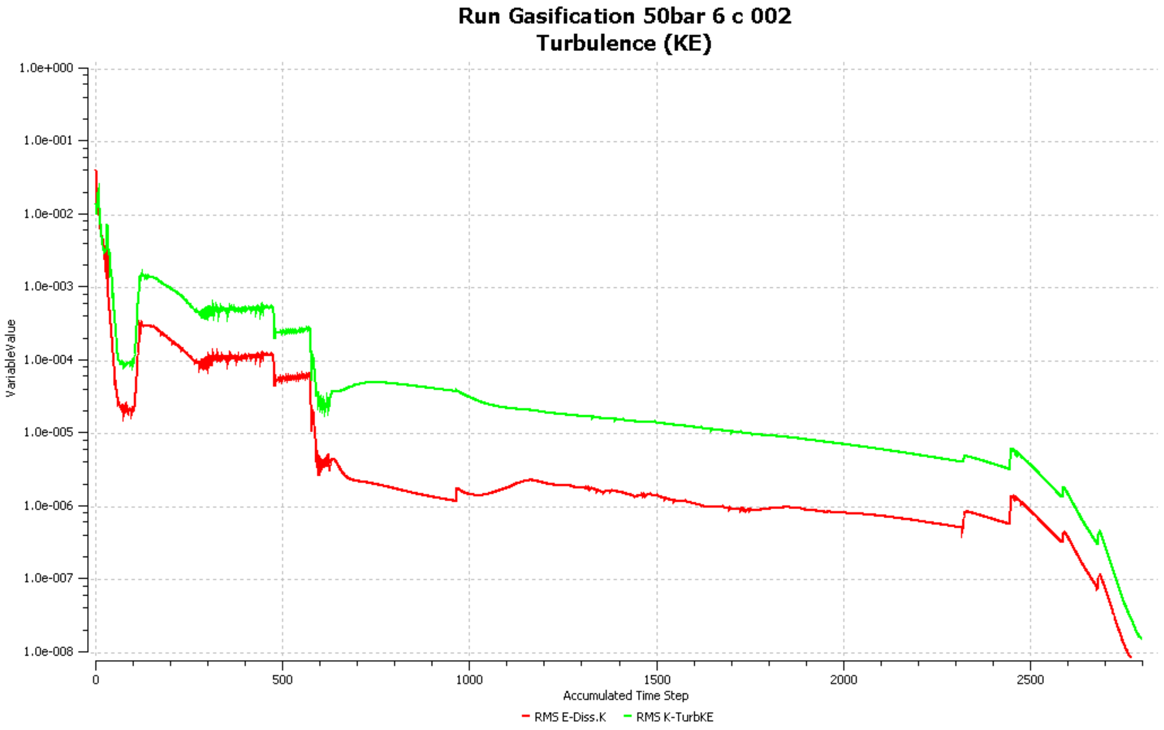


Figure 18.Residual of the solution of turbulence equations

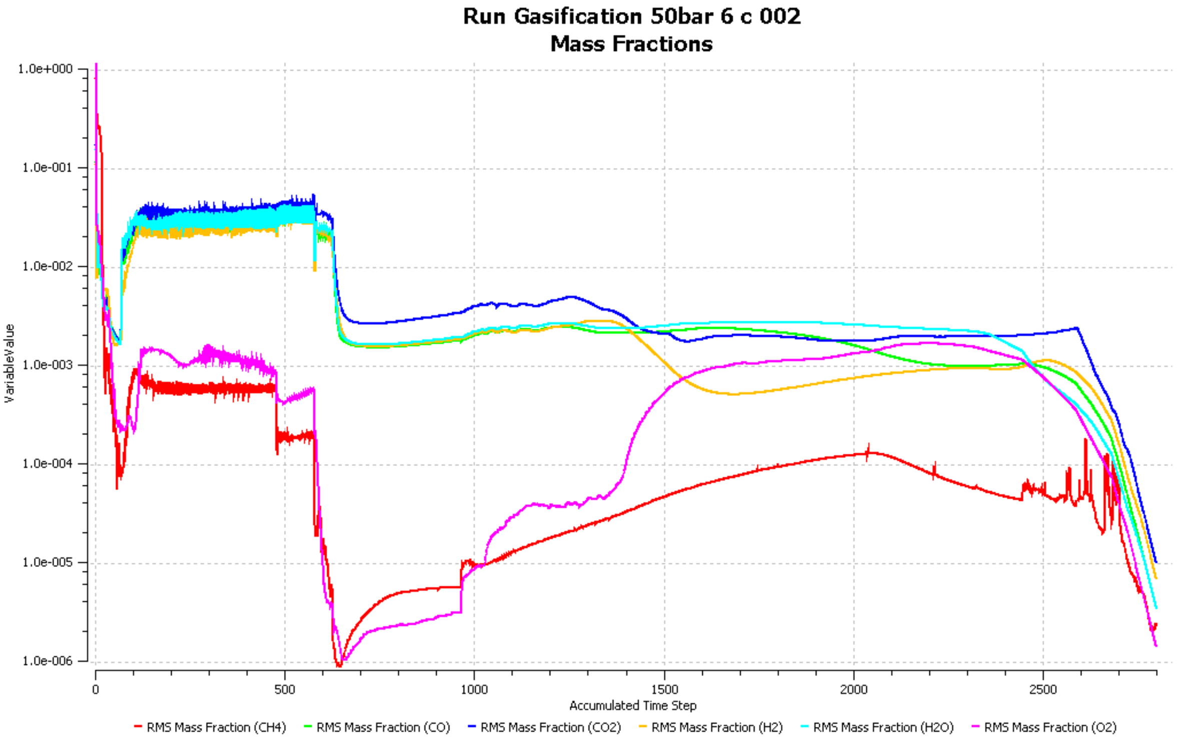


Figure 19.Residuals of the solution of the mass fraction equations

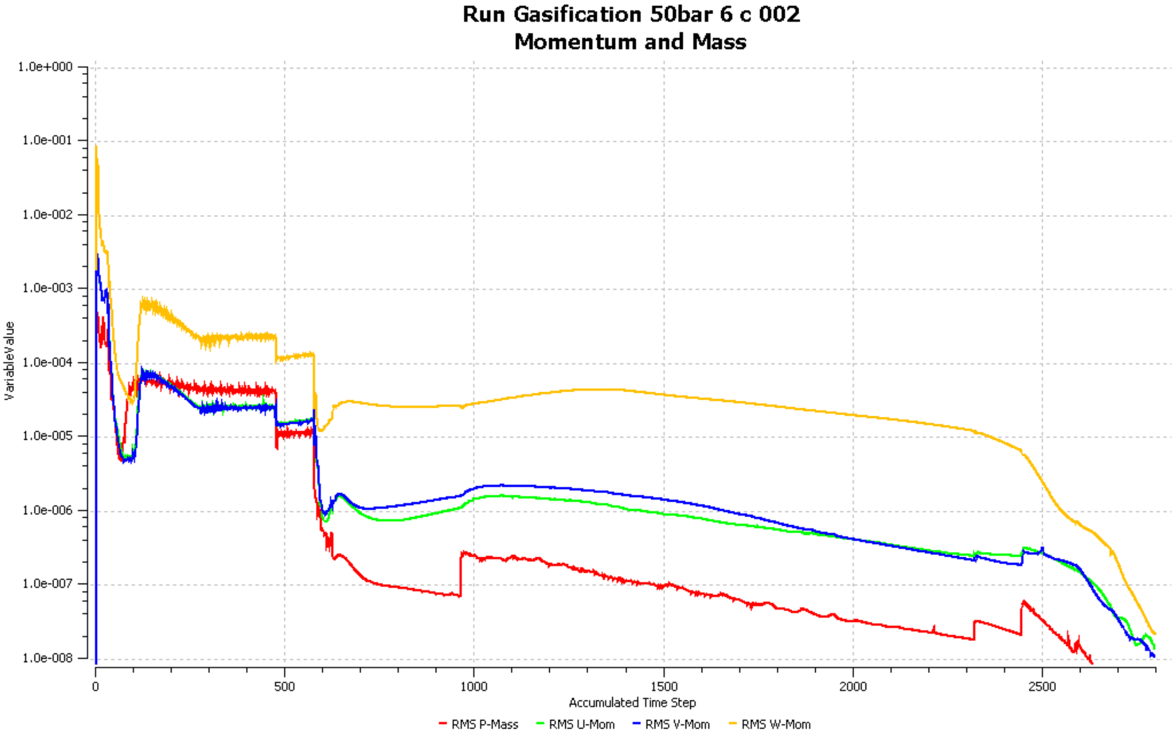


Figure 20.Residuals of the solution of momentum and mass equations

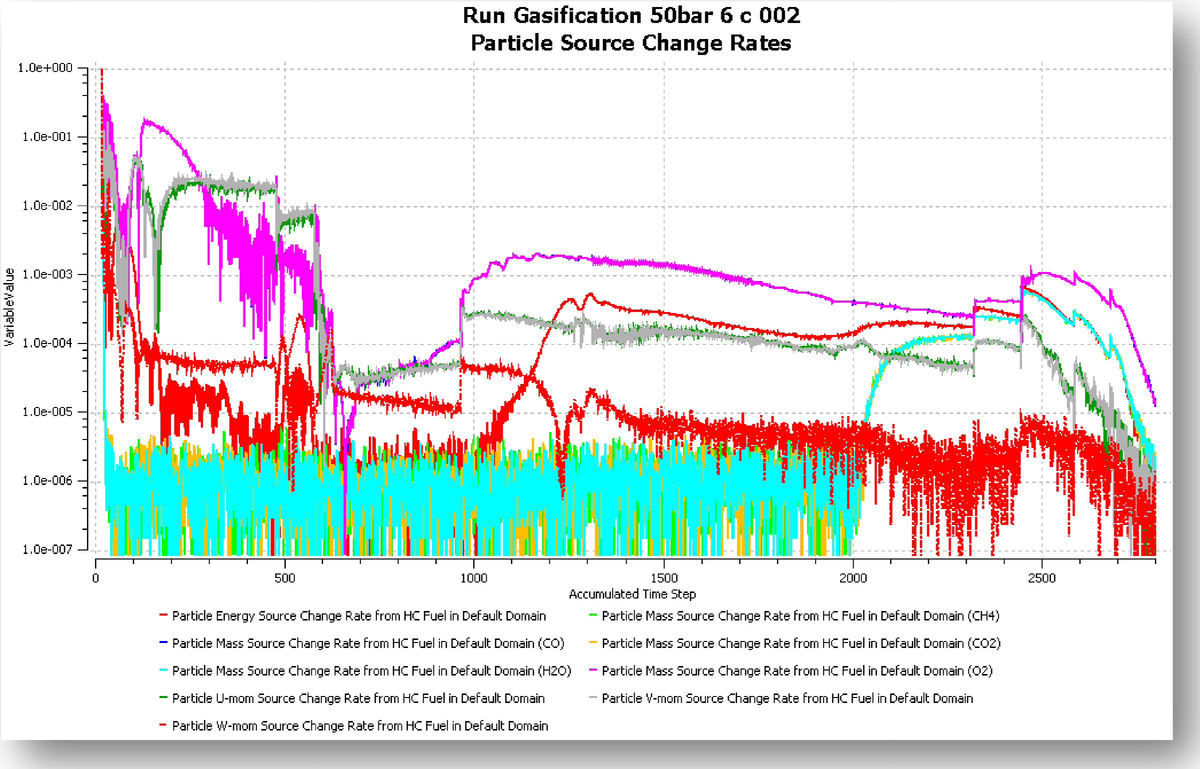


Figure 21. Particle source change rates

How the selected timestep affects the course of the solution, can be seen from the data of the following table in reference with the **Figures 17 – 21.**

Outer Loop Iteration	**1**	**31**	**475**	**575**	**623**
Timestep	1.6 E -2	3.24 E -1	1.62 E -1	3.24 E -2	3.24 E - 3
Outer Loop Iteration	**964**	**2319**	**2444**	**2584**	**2681**
Timestep	1.6 E -2	3.24 E -2	9.74 E -2	1.62 E -1	3.24 E -1

Table 15.Changes in the timestep

For the simulation at a 50 bar pressure, the time needed for the solution to converge was 1 day, 17 hours, 44 minutes and 41 seconds using a system with an Intel Pentium II 3Ghz Processor and 1,5 GB of RAM memory after 2800 iterations.

4 Results

Simulations have been conducted for pressures of 5, 25 and 50 bar. After some observations that apply for all pressure values and have to do with velocity and coal particle behavior, the results of these simulations are presented categorized by examined variable. Temperature, mass fraction and concentration of each gas contained in the final product of gasification and chemical reaction rates are the basic points of interest. The effect that pressure has on these variables is also presented.

- **General observations**

The outcome of the temperature and the methane production indicates, regardless the pressure value, the coexistence of three zones of reacting behavior of the fuel. The range of each zone is not strictly defined but there seem to be specific characteristics that can help to make the distinction among them.

- The **first zone** is the zone in which, the **mixing** of fuel with oxidant takes place. Because of their initial velocity (see Figure 22), the coal particles do not react massively with the oxidation mean and do not start to release volatiles, until they have traveled for a little more than 0.5 m inside the gasifier.
- After this length, the fuel enters what is considered to be the **second zone** inside the gasifier. It's the zone where the **gasification** of the coal particles occurs and the main quantity of methane is produced. In this zone, the oxidation reactions are the fastest and almost the whole amount of oxygen is consumed.
- In the **third zone**, gasification occurs but with slower rhythm, there are only traces of oxygen left and the dominant reactions the water-gas shift and the steam reforming.

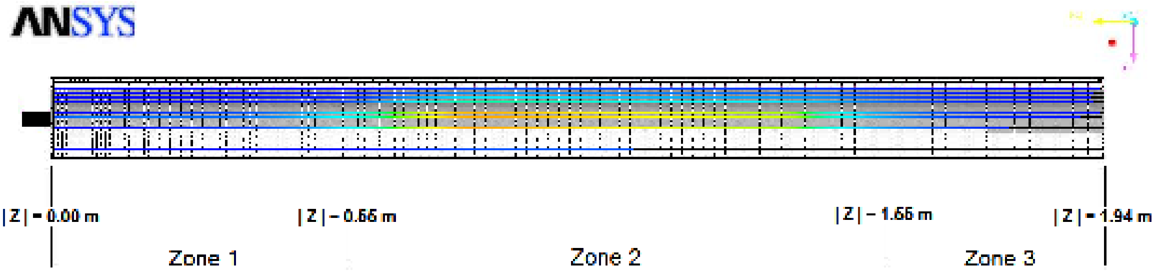


Figure 22. The zones inside the gasifier

The coal particles in all cases are moving mostly along the axis of cylindrical symmetry of the gasifier. There is no intense dispersion.

The profile of the velocity exhibits only minor fluctuations with the alteration of pressure depending to the input velocity of the gasifying agent. The gas output velocity is of the order of 0.1 m /s.

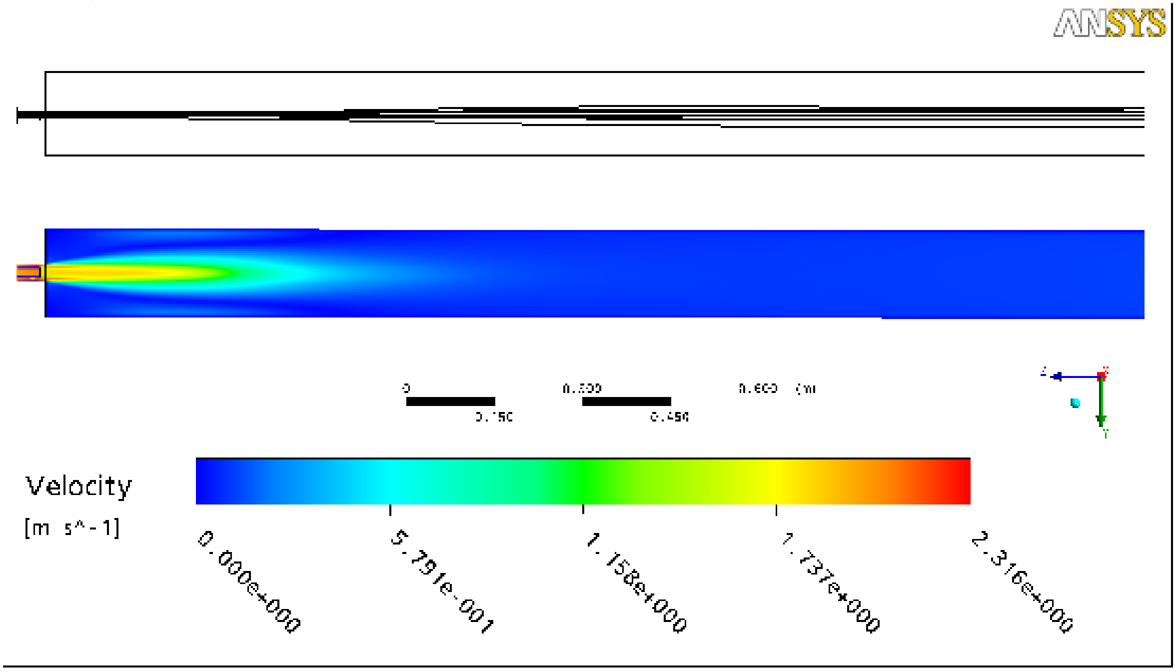


Figure 23. Coal Particle movement (up) and velocity profile (down)

4.1 Pressure 5 bar

- Max Wall Temperature: 1600 °C
- Molar fraction and concentration:

5 bar	Outlet Molar Fraction (1)	Outlet Molar Concentration [mol/m³] (2)	Outlet Molar Fraction (N_2 free)(3)
H_2	0.094	7.32	0.551
CO	0.053	3.82	0.322
CO_2	0.0004	0.039	0.003
CH_4	0.02	2.416	0.12
H_2O	0.0006	0.05	0.004
O_2	-	-	-
N_2	0.832	68.492	-
Total	1	82.137	1

Table 16. Gasification Products at 5 bar

- Reaction Rates

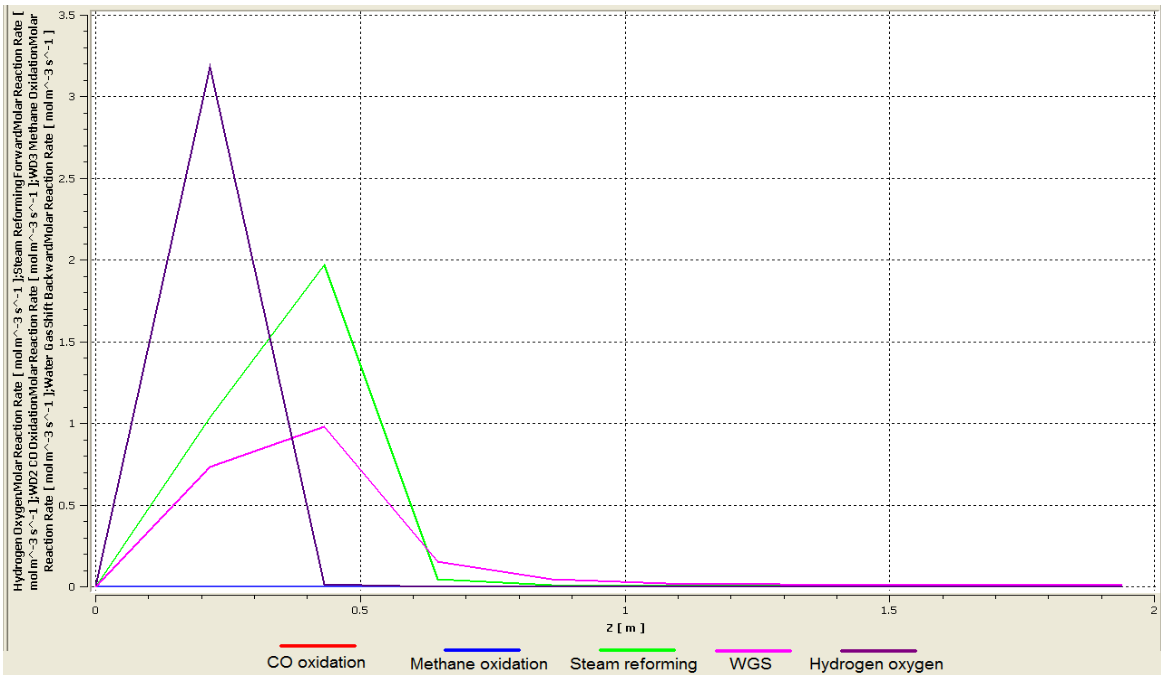


Figure 24. Reaction Rates - Gasification 5 bar

Oxygen reacts fast and is rapidly consumed. Thus the production of CO_2 and H_2O remains at low levels. Dominant reactions in the process seem to be the combustion of hydrogen, the steam reforming reaction and the water gas shift reaction.

4.2 Pressure 25 bar

- Max Wall Temperature: 1600 °C
- Molar fraction and concentration:

25 bar	Outlet Molar Fraction (1)	Outlet Molar Concentration [mol/m³] (2)	Outlet Molar Fraction (N_2 free)(3)
H_2	0.082	43.434	0.545
CO	0.046	22.798	0.306
CO_2	0.0005	0.066	0.004
CH_4	0.021	5.94	0.14
H_2O	0.0008	0.174	0.005
O_2			-
N_2	0.8497	400.788	-
Total	1	473.2	1

Table 17. Gasification Products at 25 bar

- Reaction Rates

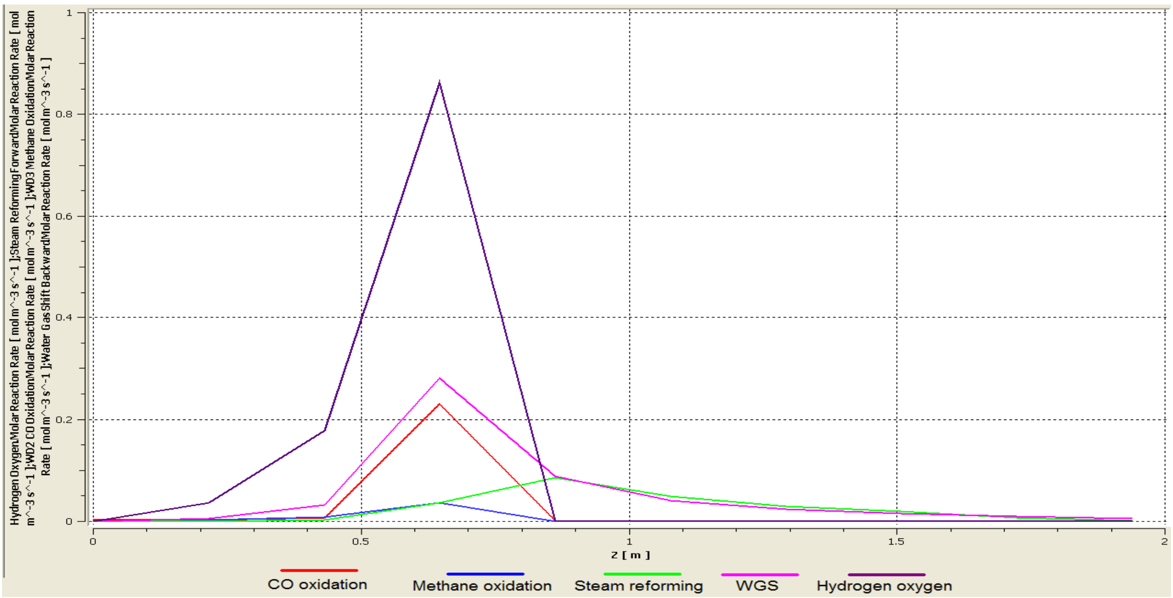


Figure 25. Reaction Rates – Gasification 25 bar

The combustion of hydrogen remains the dominant reaction. The water gas shift and the steam reforming reaction play an important role just as they did for the 5 bar pressure. The less fast consumption of oxygen has caused the increase of the CO oxidation.

4.3 Pressure 50 bar

- Max Wall Temperature: 1600 ºC
- Molar fraction and concentration:

50 bar	Outlet Molar Fraction (1)	Outlet Molar Concentration [mol/m³] (2)	Outlet Molar Fraction (N_2 free)(3)
H_2	0.076	75.323	0.54
CO	0.0428	39.276	0.302
CO_2	0.0007	0.14	0.005
CH_4	0.02	7.312	0.145
H_2O	0.0011	0.216	0.008
O_2	-	-	-
N_2	0.8594	713.159	-
Total	1	835.426	1

Table 18. Gasification products 50 bar

- Reaction Rates

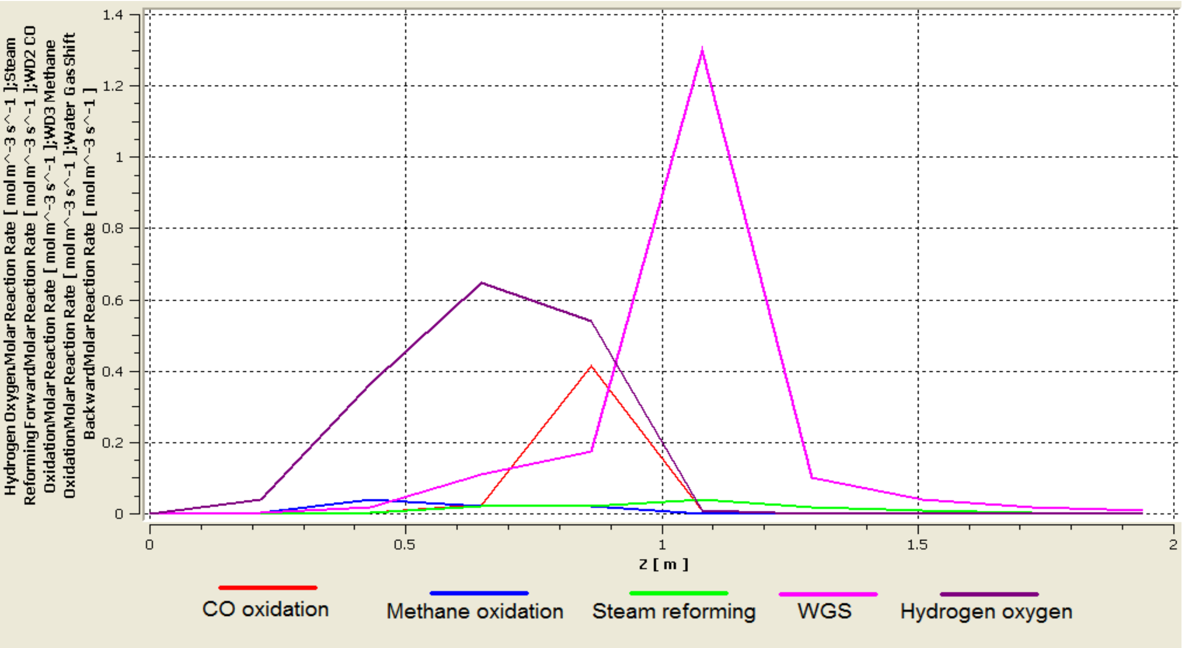


Figure 26. Reaction Rates - Gasification 50 bar

Again for the 50 bar pressure, hydrogen combustion, water gas shift and CO oxidation are the dominant reactions.

For Tables 16 17 and 18:

(1) The value of each elements molar fraction at the outlet surface.

(2) The value of each elements molar concentration at the outlet surface.

(3) The value of each elements molar fraction at the outlet surface without calculating the N2.

4.4 The effect of pressure and oxygen - fuel ratio on the final product

4.4.1 The effect of pressure

Simulations of the entrained flow gasification process were made for three different values of pressure. The effect that the change of pressure has on the gas produced is depicted on the next chart.

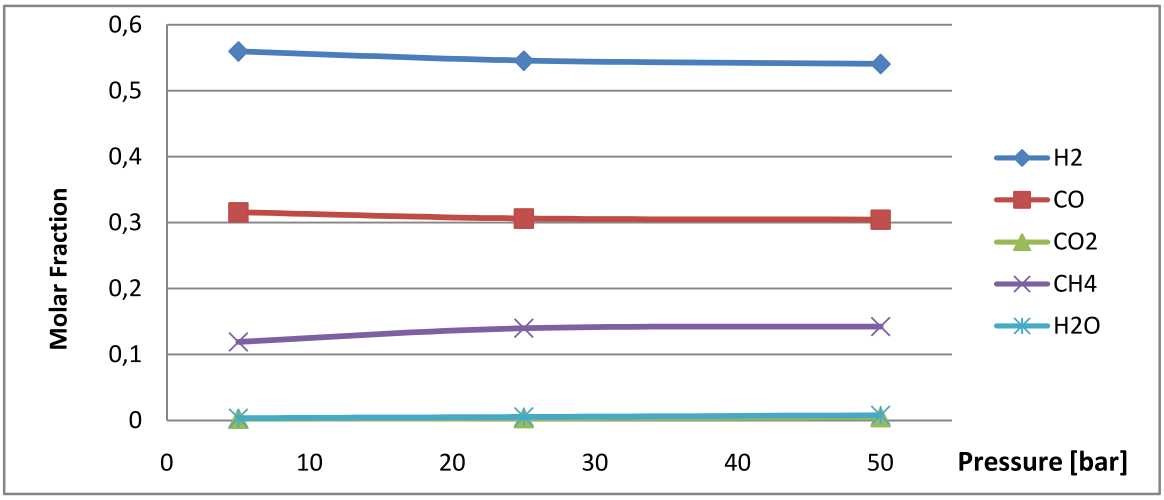


Figure 27. Molar Fraction - Pressure

As the pressure increases, the molar fractions of CO and H_2 tend to decrease. This is normal because the increase of the pressure does not favor the steam reforming reaction. Furthermore, the increase of the CH_4 molar fraction was also expected. Unexpected were the unusually low values of the CO_2 and H_2O molar fraction and high H_2 concentration in the gas produced. This is probably due to inappropriate reaction rates, but this accuracy problem can only be solved if the results are compared with actual experimental data.

4.4.2 The effect of oxygen - fuel ratio

Another variable of the gasification procedure is the ratio of oxygen and fuel that enter the gasifier. Simulations were made at the pressure of 50 bar and a fixed gasifier wall temperature of 1600ºC. Three different oxygen-fuel ratios were tested: 0.8, 0.9 and 1.0 [kg of oxygen/kg of fuel]. As shown on the figure below, on the tested area, the lower the value, the higher the concentration of CO and H_2 in the gas produced.

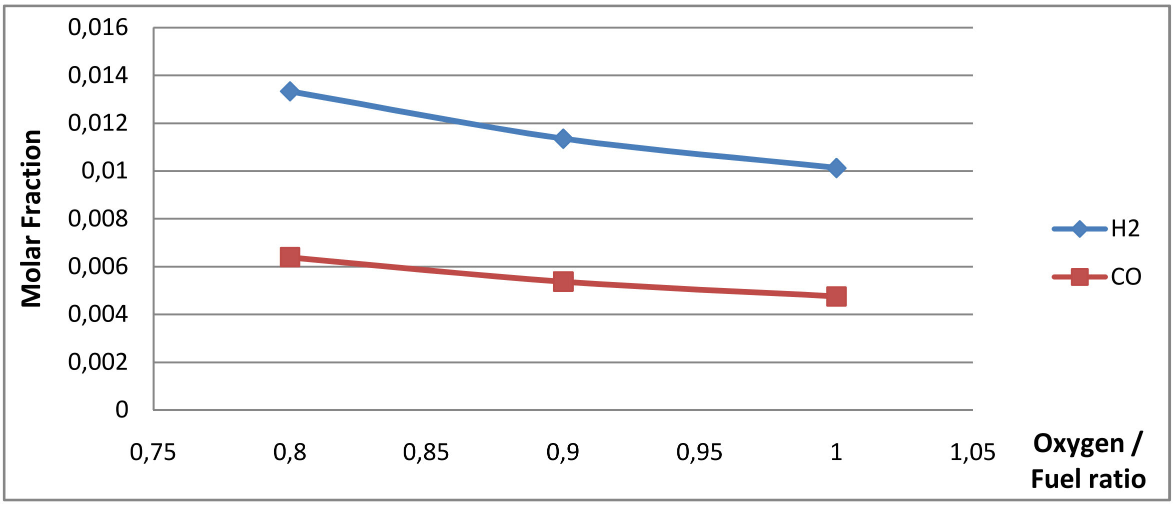


Figure 28. Molar Fraction - Oxygen/Fuel ratio

5 Conclusions

The imperative need for cleaner energy sources along with the vast global utilization of coal as a fuel, and the existence of huge infrastructure in the area of energy generation from coal-fired power plants leads to the necessity of investigating further the potential of coal.

Coal gasification, although a process initiated in the past century, it may be a step to the future and to “cleaner” energy. The hope is that the use of gasification in Integrated Gasification Combined Cycle power plants with Carbon Capture and Sequestration technology will substantially decrease the emissions of Greenhouse gases and CO_2 in particular.

The Technical University of Munich is assigned with the project of conducting the necessary research in the field of gasification and the other variables of which an IGCC power plant is consisted. As a contribution to the project, this diploma thesis develops a numerical model of entrained flow coal gasification using a commercial CFD program.

All the relative literature on the field of gasification was reviewed. The model that was developed is able to predict the composition of the gas produced from coal gasification, and other important variables such as temperature and velocity in an entrained flow gasifier. The model is realistic and is tested in various conditions of pressure and the results are satisfying. In particular: Gasification simulations were made at 5, 25 and 50 bar pressures. Some of the conclusions drew are the following:

- The variation of pressure has an effect to the hydrogen carbon monoxide production. As pressure increases, the molar fraction of these two gases decreases. However this reduction of small magnitude.
- Increasing the pressure increases the concentration of CH_4, CO_2 and H_2O but again by a small amount.
- The amount of oxygen feed is a very important variable of gasification. Surplus of oxygen results to the decrease of H_2 and CO concentration in the product gas.

Comparing the simulation results with experimental data would be necessary because, for high gasification pressures the model was tested at, the literature is poor and there are no adequate data concerning chemical reaction rates and the chemistry of gasification in general.

Further development is of course necessary if the model is targeting to be used as a mean to evaluate and optimize an existing gasifier but in a lower level of use, it can provide sufficient information for a gasifiers operation.

Appendix

Bibliography

BOOKS

- [1] A.Williams, M.Pourkashanian, J.M.Jones, N.Skorupska - Combustion and Gasification of Coal – 2000
- [2] Norbert Berkowitz – An introduction to coal technology – 1994
- [3] Bruce G. Miller – Coal energy Systems – 2005
- [4] Thomas F. Edgar – Coal processing and pollution control – 1983
- [5] L. Douglas Smoot – Fundamentals of coal combustion – 1993
- [6] D.B. Spalding – Numerical prediction of flow, heat transfer, turbulence and combustion -1983
- [7] Smoot L.D. & Smith P.J. – Coal combustion and gasification – 1985
- [8] R.W. Missen, C.A. Mims, B.A. Saville – Introduction to chemical reaction engineering and kinetics – 1999
- [9] L.D. Schmidt – The engineering of chemical reactions – 1998
- [10] John Rezaiyan N.P. Cheremisinoff – Gasification technologies: A primer for engineers and scientists – 2005
- [11] Christopher Higman, Maarten van der Burgt – Gasification – 2008
- [12] James G. Speight – Handbook of Coal Analysis – 2005

JOURNALS

- [13] Caixia Chen, Masayuki Horio, Toshinori Kojima – Numerical simulation of entrained flow coal gasifiers. Part I: modeling of coal gasification in an entrained flow gasifier. 2000
- [14] H. Watanabe, M. Otaka – Numerical simulation of coal gasification in entrained flow coal gasifier - 2006
- [15] Y.C. Choi, X. Y. Li, T.J. Park, J.H. Kim, J.G. Lee – Numerical study on the coal gasification characteristics in an entrained flow gasifier - 2001
- [16] Liang Yu, Jing Lu, X. Zhang, S. Zhang – Numerical simulation of the bubbling fluidized bed coal gasification by the kinetic theory of granular flow (KTGF) – 2006
- [17] F. Chejne, J.P. Hernandez – Modelling and simulation of coal gasification process in fluidized bed - 2002
- [18] E.M. Suuberg, W.A. Peters, J.B. Howard – Product composition and Kinetics of Lignite Pyrolysis - 1978
- [19] Peng Liang, Zhifeng Wang, Jicheng Bi – Simulation of coal pyrolysis by solid heat carrier in a moving-bed pyrolyzer – 2007
- [20] P.Quaak H.Knoef H.Stassen – Energy from Biomass – 1999

- [21] Ramid Radmanesh, Jamal Chaouki, Christophe Guy – Biomass Gasification in a Bubbling Fluidized Bed Reactor: Experiments and Modeling – 2006
- [22] Chao Chen, Edward S. Rubin – CO_2 control technology effects on IGCC plant performance and cost – 2008
- [23] John Davison – Performance and costs of power plants with capture and storage of CO_2 – 2006
- [24] Guillermo Ordorica-Garcia, Peter Douglas, Eric Croiset, Ligang Zheng – Technoeconomic evaluation of IGCC power plants for CO_2 avoidance – 2006
- [25] Mohamed Kanniche, Chakib Bouallou – CO_2 capture study in advanced integrated gasification combined cycle – 2007
- [26] C. Y. Wen, T. Z. Chaung – Entrainment Coal Gasification Modeling – 1979
- [27] Rakesh Govind, Jogen Shah – Modeling and simulation of an entrained flow coal gasifier – 1984
- [28] Andrew Charles Beath – Mathematical modeling of entrained flow coal gasification – 1996
- [29] Xiang Jun Liu, Wu Rong Zhang, Tae Jun Park – Modeling coal gasification in an entrained flow gasifier – 2001
- [30] Peter Ruprecht, Wolfgang Schafer, Paul Wallace – A computer model of entrained coal gasification – 1987
- [31] Quizhi Ni, Alan Williams – A simulation study on the performance of an entrained - flow coal gasifier – 1995
- [32] Despina Vamvuka, Edward T. Woodburn, Peter R. Senior – Modeling of an entrained flow coal gasifier 1. Development of the model and general predictions – 1995
- [33] Despina Vamvuka, Edward T. Woodburn, Peter R. Senior – Modeling of an entrained flow coal gasifier 2. Effect of operating conditions on reactor performance – 1995
- [34] G. -S. Liu, H. R. Rezaei, J. A. Lucas, D. J. Harris, T. F. Wall – Modeling of a pressurised entrained flow coal gasifier: the effect of reaction kinetics and char structure – 2000
- [35] Terry F. Wall, Gui-su Liu, Hong-wei Wu, Daniel G. Roberts, Kathy E. Benfell, Sushil Gupta, John A. Lucas, David J. Harris – The effects of pressure on coal reactions during pulverized coal combustion and gasification – 2002

INTERNET

- [36] http://www.worldcoal.org
- [37] http://en.wikipedia.org
- [38] http://criepi.denken.or.jp

- [39] http://www.netl.doe.gov
- [40] http://www.thermogenics.com
- [41] http://www.tampaelectric.com
- [42] http://www.sciencedirect.com
- [43] http://news.bbc.co.uk
- [44] http://www.futurist.com
- [45] http://www.foe.co.uk
- [46] http://www.energ.co.uk
- [47] http://www.world-nuclear.org
- [48] http://www.eia.doe.gov
- [49] http://www.gepower.com
- [50] http://www.cleansolutionsco.com
- [51] http://www.inl.gov
- [52] www.volund.dk
- [53] www.xylowatt.com
- [54] http://www.wri.org
- [55] www.greentechnolog.com
- [56] www.vattenfall.com