EARLY ENTRANCE COPRODUCTION PLANT

PHASE II

Topical Report

Task 2.7: Petroleum Coke Analysis

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Disclaimer

Abstract

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which produces at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology. The objective of Phase I is to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan to mitigate technical risks and barriers; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site.

The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation. The partners in this project are TES (a subsidiary of ChevronTexaco), General Electric (GE), Praxair, and Kellogg Brown & Root (KBR) in addition to the U.S. Department of Energy (DOE). TES is providing gasification technology and Fischer-Tropsch (F-T) technology developed by Rentech, GE is providing combustion turbine technology, Praxair is providing air separation technology, and KBR is providing engineering.

Each of the EECP subsystems were assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The RD&T Plan identified petroleum coke characteristics as a potential technical risk. The composition of petroleum coke varies from one refinery to another. Petroleum coke characteristics are a function of the crude oil slate available at the refinery and the coker operating parameters. The specific petroleum coke characteristics at a refinery affect the design of the Gasification and Acid Gas Removal (AGR) subsystems. Knowing the petroleum coke composition provides the necessary data to proceed to the EECP Phase III engineering design of the gasification process. Based on ChevronTexaco's experience, the EECP team ranked the technical, economic, and overall risks of the petroleum coke composition related to the gasification subsystem as low.

In Phase I of the EECP Project, the Motiva Port Arthur Refinery had been identified as the potential EECP site. As a result of the merger between Texaco and Chevron in October 2001, Texaco was required to sell its interest in the Motiva Enterprises LLC joint venture to Shell Oil Company and Saudi Refining Inc. To assess the possible impact of moving the proposed EECP host site to a ChevronTexaco refinery, samples of petroleum coke from two ChevronTexaco refineries were sent to MTC for bench-scale testing. The results of the analysis of these samples were compared to the Phase I EECP Gasification Design Basis developed for Motiva's Port Arthur Refinery. The analysis confirms that if the proposed EECP is moved to a new refinery site, the Phase I EECP Gasification Design Basis would have to be updated. The lower sulfur content of the two samples from the ChevronTexaco refineries indicates that if one of these sites were selected, the Sulfur Recovery Unit (SRU) might be sized smaller than the current EECP design. This would reduce the capital expense of the SRU. Additionally, both ChevronTexaco samples have a higher hydrogen to carbon monoxide ratio than the Motiva Port Arthur petroleum coke. The higher hydrogen to carbon monoxide ratio could give a slightly higher F-T products

yield from the F-T Synthesis Reactor. However, the EECP Gasification Design Basis can not be updated until the site for the proposed EECP site is finalized. Until the site is finalized, the feedstock (petroleum coke) characteristics are a low risk to the EECP project.

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The Contractor can not confirm the authenticity of the information contained herein since this report is being submitted under the U.S. Department of Energy requirement that the electronic files must be submitted without being write-protected.

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Executive Summary

This report summarizes Task 2.7: Petroleum Coke Analysis of Phase II of the development of the Early Entrance Coproduction Plant (EECP) being performed under U.S. Department of Energy (DOE) Cooperative Agreement No. DE-FC26-99FT40658. The EECP will integrate advanced high efficiency, fuel flexible electrical power generation (gasification) from coal or other carbonaceous material with a coproduction facility capable of producing clean transportation fuels and/or chemicals. An industrial consortium consisting of Texaco Energy Systems Inc. (TES), Kellogg Brown & Root (KBR), General Electric (GE), Praxair, and Rentech is developing this project.

The overall objective of this project is the three phase development of an Early Entrance Coproduction Plant (EECP) which uses petroleum coke to produce at least one product from at least two of the following three categories: (1) electric power (or heat), (2) fuels, and (3) chemicals using ChevronTexaco's proprietary gasification technology. The objective of Phase I was to determine the feasibility and define the concept for the EECP located at a specific site; develop a Research, Development, and Testing (RD&T) Plan for implementation in Phase II; and prepare a Preliminary Project Financing Plan. The objective of Phase II is to implement the work as outlined in the Phase I RD&T Plan to enhance the development and commercial acceptance of coproduction technology. The objective of Phase III is to develop an engineering design package and a financing and testing plan for an EECP located at a specific site. The project's intended result is to provide the necessary technical, economic, and environmental information needed by industry to move the EECP forward to detailed design, construction, and operation.

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The EECP converts petroleum coke into synthesis gas in the Gasification section. Approximately 1,120 metric tons (1,235 short tons per day) petroleum coke is used to produce 55 megawatts of net electric power for export, approximately 617 barrels per day of Fischer-Tropsch (F-T) products (finished high-melt wax, finished low-melt wax, F-T diesel, and F-T naphtha), steam, and approximately 81 metric tons (89 short tons per day) of sulfur. Additionally, the Air Separation Unit (ASU) will produce nitrogen and oxygen for export.

Each of the EECP subsystems were assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The RD&T Plan identified the petroleum coke characteristics as a potential technical risk. The composition of petroleum coke varies from one refinery to another. Knowing the petroleum coke composition provides the necessary data to proceed to the EECP Phase III engineering design of the gasification process. Based on ChevronTexaco's experience, the EECP team ranked the technical, economic, and overall risks of the petroleum coke composition related to the gasification subsystem as low.

Petroleum coke characteristics are a function of the crude oil slate available at the refinery and the coker operating parameters. The specific petroleum coke characteristics at a refinery affect the design of the Gasification and Acid Gas Removal (AGR) subsystems. Analysis of the petroleum coke at ChevronTexaco's Montebello Technology Center (MTC), Montebello, California included ultimate analysis and gross heating value.

In Phase I of the EECP Project, the Motiva Port Arthur Refinery had been identified as the potential EECP site. As a result of the merger between Texaco and Chevron in October 2001, Texaco was required to sell its interest in the Motiva Enterprises LLC joint venture to Shell Oil Company and Saudi Refining Inc. To assess the possible impact of moving the proposed EECP host site to a ChevronTexaco refinery, samples of petroleum coke from two ChevronTexaco refineries were sent to MTC for bench-scale testing. The results of the analysis of these samples were compared to the Phase I EECP Gasification Design Basis developed for Motiva's Port Arthur Refinery. The analysis confirms that if the proposed EECP is moved to a new refinery site, the Phase I EECP Gasification Design Basis would have to be updated. The lower sulfur content of the two samples from the ChevronTexaco refineries indicates that if one of these sites were selected by the team, the Sulfur Recovery Unit (SRU) might be sized smaller than the current EECP design. This would reduce the capital expense of the SRU. Additionally, both ChevronTexaco samples have a higher hydrogen to carbon monoxide ratio than the Motiva Port Arthur petroleum coke. The higher hydrogen to carbon monoxide ratio could give a slightly higher F-T products yield from the F-T Synthesis Reactor. However, the EECP Gasification Design Basis can not be updated until the site for the proposed EECP site is finalized. Until the site is finalized, the feedstock (petroleum coke) characteristics are a low risk to the EECP project.

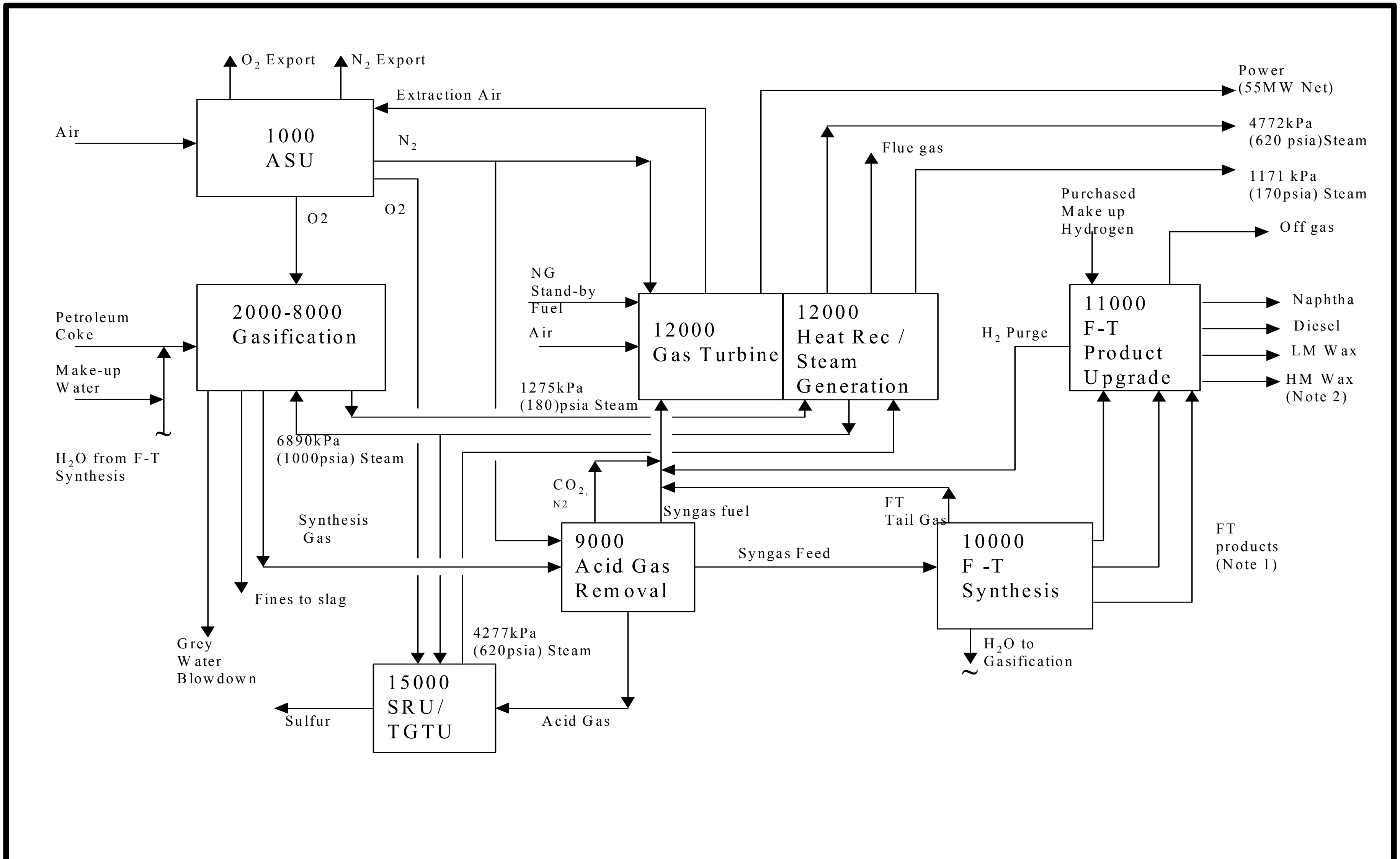
Background

The proposed EECP facility will coproduce electric power and steam for export and internal consumption, finished high-melt wax, finished low-melt wax, Fischer-Tropsch (F-T) diesel, F-T naphtha, elemental sulfur, and will consume approximately 1,235 short tons per day of petroleum coke. The EECP Concept is illustrated in Schematic 1.

Petroleum coke is ground, mixed with water and pumped as thick slurry to the Gasification Unit. This coke slurry is mixed with high-pressure oxygen from the Air Separation Unit (ASU) and a small quantity of high-pressure steam in a specially designed feed injector mounted on the gasifier. The resulting reactions take place very rapidly to produce synthesis gas, also known as syngas, which is composed primarily of hydrogen, carbon monoxide, water vapor, and carbon dioxide (CO_2) with small amounts of hydrogen sulfide, methane, argon, nitrogen, and carbonyl sulfide. The raw syngas is scrubbed with water to remove solids, cooled, and then forwarded to the Acid Gas Removal Unit (AGR), where the stream is split. Approximately 75% of the synthesis gas is treated in the AGR to remove the bulk of H_2S with minimal CO_2 removal and then forwarded as fuel to the GE frame 6FA gas turbine. The remaining 25% of the stream is treated in the AGR to remove CO_2 and H_2S and then passed through a zinc oxide bed arrangement to remove the remaining traces of sulfur before being forwarded to the F-T Synthesis Unit. In the AGR solvent regeneration step, high pressure nitrogen from the ASU is used as a stripping agent to release CO_2. The resulting CO_2 and nitrogen mixture is also sent to the gas turbine, which results in increased power production and reduced nitrogen oxides emissions. The bulk of the nitrogen from the air separation unit is sent to the gas turbine as a separate stream and combined in the combustion chamber with the syngas fuel to increase the power production and reduce nitrogen oxide emissions from the gas turbine.

In the F-T reactor, carbon monoxide and hydrogen react, aided by an iron-based catalyst, to form mainly heavy straight-chain hydrocarbons. Since the reactions are highly exothermic, cooling coils are placed inside the reactor to remove the heat released by the reactions. Three hydrocarbon product streams, heavy F-T liquid, medium F-T liquid and light F-T liquid are sent to the F-T product upgrading unit while F-T water, a reaction byproduct, is returned to the Gasification Unit. The F-T tail gas and AGR off gas are fed to the gas turbine and mixed with syngas. This increases electrical power production by 11%.

In the F-T Product Upgrading Unit (F-TPU), the three F-T liquids are combined and processed as a single feed. In the presence of a hydrotreating catalyst, hydrogen reacts slightly exothermally with the feed to produce saturated hydrocarbons, water, and some hydrocracked light ends. The resulting four liquid product streams are naphtha, diesel, low-melt wax, and high-melt wax that leave the EECP facility via tank truck.



Kellogg Brown & Root, Inc.
A Halliburton Company
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Technical Services, Inc.

NOTES:

1. Includes Light, Medium and Heavy FT Liquid product streams
2. LM = Low Melt
   HM = High Melt

DOE EARLY ENTRANCE COPRODUCTION PLANT
PORT ARTHUR REFINERY

OVERALL BLOCK FLOW DIAGRAM

DRAWN JSA	DATE 10/10/0	DOE AWARD NUMBER: DE-FC-99FT40658	REV.
DESIGNER	DATE	SUBCONTRACTOR PROJECT NO: 9202	0
CHECKED	DATE	TASK NO: 4.1.2	
APPROVED	DATE	DRAWING NO: KBR-P-BFD-0001	

Schematic 1 – EECP Concept

The power block consists of a GE PG6101 (6FA) 60 Hertz (Hz) heavy-duty gas turbine generator and is integrated with a two-pressure level heat recovery steam generator (HRSG) and a non-condensing steam turbine generator. The system is designed to supply a portion of the compressed air feed to the ASU, process steam to the refinery, and electrical power for export and use within the EECP facility. The gas turbine has a dual fuel supply system with natural gas as start-up and backup fuel, and a mixture of syngas from the gasifier, offgas from the AGR Unit, and tail gas from the F-T Synthesis Unit as the primary fuel. Nitrogen gas for injection is supplied by the ASU for nitrogen oxides (NOx) abatement, power augmentation, and the fuel purge system.

The Praxair ASU is designed as a single train elevated pressure unit. Its primary duty is to provide oxygen to the gasifier and Sulfur Recovery Unit (SRU), and to satisfy all of the EECP's requirements for nitrogen, instrument air, and compressed air. Nitrogen produced by the ASU is used within the EECP as a stripping agent in the AGR Unit, as diluents in the gas turbine where its mass flow helps increase power production and reduce NOx emissions, and as an inert gas for purging. The gas turbine, in return for diluent nitrogen, supplies approximately 25% of the air feed to the ASU, which helps reduce the size of the ASU's air compressor and oxygen supply cost.

Acid gases from the AGR, as well as sour water stripper (SWS) off gas from the Gasification Unit, are first routed to knockout drums and then to the Claus SRU. After entrained liquid is removed in these drums, the acid gas is preheated and fed along with the SWS off gas, oxygen, and air to a burner. In the thermal reactor, the hydrogen sulfide (H_2S), a portion of which has been combusted to sulfur dioxide (SO_2), starts to recombine with the SO_2 to form elemental sulfur. The reaction mixture then passes through a boiler to remove heat while generating steam. The sulfur-laden gas is sent to the first pass of the primary sulfur condenser where all sulfur is condensed. The gas is next preheated before entering the first catalytic bed in which more H2S and SO_2 are converted to sulfur. The sulfur is removed in the second pass of the primary sulfur condenser, and the gas goes through a reheat, catalytic reaction, and condensing stage two more times before leaving the SRU as a tail gas. The molten sulfur from all four condensing stages is sent to the sulfur pit, from which sulfur product is transported off site by tank truck.

The tail gas from the SRU is preheated and reacted with hydrogen in a catalytic reactor to convert unreacted SO_2 back to H2S. The reactor effluent is cooled while generating steam before entering a quench tower for further cooling. A slip stream of the quench tower bottoms is filtered and sent along with the condensate from the SRU knockout drums to the SWS. H_2S is removed from the quenched tail gas in an absorber by using lean methyldiethanolamine (MDEA) solvent from the AGR Unit. The tail gas from the absorber is thermally oxidized and vented to the atmosphere. The rich MDEA solvent returns to the AGR Unit to be regenerated in the stripper.

During Phase I, each of the EECP subsystems was assessed for technical risks and barriers. A plan was identified to mitigate the identified risks (Phase II RD&T Plan, October 2000). The RD&T Plan identified petroleum coke characteristics as a potential technical risk. The composition of petroleum coke varies from one refinery to another. Knowing the petroleum coke composition provides the necessary data to proceed to the EECP Phase III engineering design of the gasification process. Based on ChevronTexaco's experience, the EECP team ranked the technical, economic, and overall risks of the petroleum coke composition related to the gasification subsystem as low.

Samples of petroleum coke from Motiva Port Arthur were sent to ChevronTexaco's Montebello Technology Center (MTC) for analysis. As a result of the merger between Texaco and Chevron in October 2001, Texaco was required to sell its interest in the Motiva Enterprises LLC joint venture to Shell Oil Company and Saudi Refining Inc. The team acquired petroleum coke samples from ChevronTexaco refineries for analysis to help assess the impact of moving the proposed EECP to a ChevronTexaco refinery.

Petroleum Coke Analysis

Petroleum coke samples were analyzed at ChevronTexaco MTC. Table 1 summarizes the differences between the three samples. Samples from the two ChevronTexaco refineries, identified as Refinery A and Refinery B, have higher carbon and hydrogen and lower sulfur amounts by weight percent (wt%) basis compared to the Motiva Port Arthur petroleum coke. Also, the gross heating value of the Motiva Port Arthur petroleum coke is less than that of the two ChevronTexaco Refineries.

Petroleum Coke Characteristics

Charge to Gasifier	**EECP Phase I Design Conditions**	**Motiva Port Arthur (Typical)**	**ChevronTexaco Refinery A**	**ChevronTexaco Refinery B**
Ultimate Analysis, wt%, dry basis				
Carbon	88.61	88.61	89.43	89.74
Hydrogen	2.80	2.80	4.14	4.29
Nitrogen	1.10	1.06	1.05	1.08
Sulfur	8.00 Max	7.30	5.08	4.60
Oxygen	0.00	0.00	0.00	0.00
Ash	0.40 Max	0.23	0.39	0.29
Moisture as Received, wt%	9	8.37	10.07	9.31
Chloride Content, parts per million (ppm) by weight, dry basis	50 max	20	<5	23
Gross Heating Value, KJ/KG (Btu/lb), Dry Basis	34536 (14,848)	34536 (14,848)	35,504 (15,264)	35,658 (15,330)

The differences in the petroleum coke samples will result in the team updating the EECP gasification design conditions. For example, the lower sulfur content of the two ChevronTexaco refineries can lead to a reduction in the capital costs of the sulfur recovery unit. The higher hydrogen to carbon ratio of the two ChevronTexaco refinery petroleum coke samples should result in slightly higher hydrogen to carbon monoxide ratio in the synthesis gas. This could improve the yield of the F-T Synthesis Reactor. The lower sulfur content and higher hydrogen content could improve the overall EECP economics. However, any update of the design conditions must be location specific. Therefore, the team will select an EECP site in Task 4: Update the Concept Basis of Design. After a suitable location has been selected, the team will initiate the update of the concept design basis. The location for the proposed EECP will be based on the availability of a low cost feedstock such as petroleum coke and integration potential with the proposed EECP (i.e. the location has a need for power, steam, and/or F-T products).

Conclusions

Petroleum coke varies from refinery to refinery. Its composition is based on the refinery crude slate and coker feed and operating conditions. The sale of Texaco's interest in the Motiva Enterprises joint venture with Shell and Saudi Refining has caused the team to begin evaluating new sites for the proposed EECP. Petroleum coke samples from two ChevronTexaco refineries were analyzed and compared to the EECP design conditions. Both samples have a higher hydrogen content, higher gross heating value, and lower sulfur content than the Motiva Port Arthur petroleum coke. The lower sulfur content could allow for a smaller SRU in the EECP. This would lower the overall capital expense required for the EECP. However, the design basis can not be updated until a suitable EECP site is identified by the EECP team. Once the site is selected, the EECP Phase I Gasification Design Basis will be updated to reflect the feedstock characteristics of that specific site. The site will be selected based on its availability of a low cost feedstock such as petroleum coke and the integration potential with the EECP. Until the site is finalized, the feedstock (petroleum coke) characteristics are a low risk to the EECP project.

Bibliography

J. S. Falsetti and R. L. Skarbek, "Petroleum Coke Utilization with the Texaco Gasification Process", *National Petroleum Refiners Association*, AM-93-71, 1993 NPRA Annual Meeting, March 1993.

List of Acronyms and Abbreviations

AGR	Acid Gas Removal
ASU	Air Separation Unit
Btu	British thermal unit
CO_2	Carbon Dioxide
DOE	Department of Energy
EECP	Early Entrance Coproduction Plant
F-T	Fischer-Tropsch
F-TPU	Fischer-Tropsch Product Upgrading
GE	General Electric
H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen Sulfide
HRSG	heat recovery steam generator
KBR	Kellogg Brown & Root
KG	Kilogram
KJ	Kilojoule
kPa	kilopascal
lb	pound
MDEA	methyldiethanolamine
MTC	Montebello Technology Center
MW	Megawatt
N_2	Nitrogen
NG	Natural Gas
O_2	Oxygen
ppm	parts per million
psia	pounds per square inch - atmosphere
RD&T	Research, Development, and Testing
SO_2	Sulfur Dioxide
SRU	Sulfur Recovery Unit
SWS	Sour Water Stripper
TES	Texaco Energy Systems LLC
wt%	weight percent