

PN-AA4-592
40993

STATE-OF-THE-ART REVIEW ON THE PRODUCTION OF METHANOL AND ITS DERIVATIVES FROM BIOMASS

Final Report

July 1981

By: Anil K. Chatterjee, P.E.

B.K.Chatterjee
P.R.Chatterjee

Prepared For:

**UNITED STATES DEPARTMENT OF AGRICULTURE
Foreign Agriculture Service
Washington, D.C.**

**Contract NO. 53-319R-1-216
AC Project- P015/2**

**Anil K. Chatterjee, P.E.
Engineering Consultant
4883 Windermere Drive
Newark, California 94560
(415) 796-5436**

CONTENTS

	Page
LIST OF ILLUSTRATIONS.....	iii
LIST OF TABLES.....	iv
ACKNOWLEDGEMENTS.....	v
I. INTRODUCTION.....	1
II. EXECUTIVE SUMMARY.....	4
III. OBJECTIVE AND SCOPE OF STUDY.....	9
IV. BACKGROUND.....	10
A. Historical Review.....	10
B. Literature Search.....	14
C. Feedstock Preparation.....	15
V. PROCESS DESCRIPTION.....	21
A. Synthesis Gas Production.....	21
1. Flow Diagram.....	21
2. Equipment System.....	27
3. Mass Balance.....	33
B. Methanol Synthesis Processes.....	36
1. Chem. System Process.....	37
2. ICI Process.....	41
3. Lurgi Process.....	46
C. Methanol Derivatives.....	53
1. Mobil Process.....	53
2. China Lake Process.....	54
VI. HEALTH AND ENVIRONMENTAL CONSIDERATIONS.....	55
VII. GASIFIER DESIGN CRITERIA AND AVAILABLE DESIGNS.....	59
VIII. ESTIMATED INVESTMENT COST (U.S.A. BASIS).....	67

	Page
IX. BASE CASE PRODUCT AND OPERATING COST.....	72
X STATUS OF PROCESS DEVELOPMENT.....	77
XI. APPLICABILITY TO LDCs.....	80
XII. LIST OF OTHER SOURCES IN THE FIELD.....	82
XIII. SUMMARY OF FINDINGS.....	85
XIV. RECOMMENDATIONS.....	87
APPENDIX	
A. References.....	89
B. Ackronyms/Symbols/Abbreviations.....	91

LIST OF ILLUSTRATIONS

	Page
1. Typical Rotary Dryer System.	17
2. Single-Train Residue Pelletizing Plant.	19
3. Principal Reaction Paths in Biomass Gasification.	22
4. Flow Diagram for Direct Gasification of Biomass.	23
5. Typical Flow Diagram for Methanol Synthesis.	34
6. Chem Systems Synthesis Flow Diagram.	38
7. ICI Flow Diagram.	44
8. Lurgi Tubular Reactor.	47
9. Lurgi Flow Diagram.	47
10. Modernized Single-Stage Fixed Bed Gasifier.	62
11. Two-Stage Fixed Bed Gasifier.	64
12. Comparison of Investment Requirements for 50 and 200 Million gpy Methanol Plants.	70

LIST OF TABLES

	Page
1. Chem Systems Synthesis- Material Balance.	35
2. Chem Systems Synthesis- Energy Balance.	35
3. Properties of Chem Systems Methanol Fuel.	40
4. Comparison of Chem Systems Synthesis at Two Pressures.	42
5. Lurgi's Methanol Properties.	51
6. Comparison of Low Pressure Systems.	52
7. Estimated Methanol Tolerance Levels.	57
8. Estimated Investment Cost Summary.	67
9. Detailed Cost Analysis.	68
10. Operating Cost Estimate for 50 Million gpy Methanol Plant.	73
11. Comparison of Methanol Selling Price.	75
12. Cost Estimate of Fuels Derived From Thermochemical Processes.	76
13. Distribution of World Methanol Plants.	78
14. Low Pressure Plants Licensed by ICI.	83
15. Gasification Plants Using Biomass.	84

ACKNOWLEDGEMENTS

This report represents the results of the state-of-the-art review of the production of methanol from biomass for the U.S. Department of Agriculture Foreign Agriculture Service, by Anil K. Chatterjee, P.E. Engineering consultant.

Mr. Jeff Mawer, Vice President Process and Mr. Stewart Brown, Vice President of Sales for DM International, Houston operation supplied valuable information concerning their methanol projects around the globe. Mr. Ron Enzweilr of Lurgi Corporation, Belmont, Ca, supplied information on the Lurgi synthesis process.

Mr. Bikash K. Chatterjee, helped me in the literature search, energy and mass balance calculations, and methanol synthesis technology research write-up and editing of the text. Mr. Pallab R. Chatterjee helped in the coordinating and preparation of the final report.

Dr. Harold E. Wahlgren, Leader, Bio-resources for Energy Project, USDA, Forest Service was the principal officer and Dr. Jack Fritz of A.I.D. Washington, D.C. served as advisor for the project.

I.

INTRODUCTION

This state-of-the-art review of the production of methanol from biomass was performed by Anil K. Chatterjee, P.E. for the United States Department of Agriculture (USDA), under contract 53-319R-1-216, dated May 15, 1981. The study covered the following major steps:

- * Historical background
- * Process description of synthesis gas production from biomass feedstock.
- * Secondary conversion of synthesis gas to fuel grade methanol by various methanol synthesis processing.
- * Discussions on gasifier designs.
- * Economic base.
- * Product utilization.
- * Status of process development.
- * Summary of findings.

Any carbonaceous material such as coal, lignite, any lignocellulosic materials like wood waste and agricultural residue, and even cellulosic solid waste can be utilized for synthetic methanol production ¹. At present commercial production of methanol is exclusively from natural gas.

Natural gas is first reformed to synthesis gas and after the H₂ to CO ratio is adjusted in composition, it is synthesized to methanol ².

The general argument for converting biomass to methanol, is that methanol can be used as transportation fuel and other applications ².

- * As a fuel supplement to automotive engines.
- * As a fuel replacement for steam generator and gas turbine engines.
- * As feedstock to produce gasoline.
- * For use in metallurgical furnaces as a reducing gas.
- * For use in fuel cells or as a source of hydrogen generation.
- * For industrial chemical products like plastics, synthetic fibers, fertilizer, herbicides and solvents².
- * For reconversion to synthetic natural gas (SNG) at another location.
- * As a biological feedstock for protein.

The concept of using methanol as a gasoline replacement for automobiles is quite attractive and many developing nations are now interested in such conversion technology. Brazil with her large biomass resources has undertaken ambitious programs for producing methanol from the country's forestry resources. They have already developed an automotive engine that burns methanol efficiently as an automotive fuel.

The results of an investigation undertaken by the Ford Motor Corp., utilizing engines which take advantage of methanol's high compression ratio, indicated that a 12.5 percent reduction in overall cost would be achieved using chemical grade methanol as a fuel supplement. In addition, engine life was doubled using methanol as a fuel. The savings in engine wear was deemed more than sufficient to compensate for the cost of retrofitting engines to utilize the

higher compression ratio. These savings were based on a market price of 88¢/gal (23¢/liter) for methanol and \$1.23/gal (32¢/liter) for gasoline ³.

It has been projected that on a delivered energy basis, and without special government aid, methanol may be produced for 25 to 35¢/gal (7-9¢/liter) ³.

In addition, recent improvements in the technology of methanol catalysts has decreased overall plant costs by 18 percent. This corresponds to a reduction of 12.5¢/gal (3.3¢/liter) in the cost of methanol ³.

All of these factors further decreases the net cost of methanol production and makes it a more attractive automobile fuel substitute for gasoline.

Combustion turbines, with a power cycle burning methanol, built by Westinghouse, General Electric, and United Technologies, have demonstrated a one-third higher thermal efficiency when compared to normal coal-fired steam turbines. A steam power plant will generally take twice as long to build and will require approximately twice the cost of a methanol plant ³.

Thus as methanol production technologies advance, so will the advantages of methanol as a fuel substitute, especially as a gasoline substitute.

II. EXECUTIVE SUMMARY

General

As the cost of liquid and gaseous fuels increases and subsequently create a greater economic burden on many developing countries, the use of alternate sources of energy, such as biomass, is becoming increasingly attractive. One of the largest economic burdens is created by the importation of gasoline.

Process

Any carbonaceous material, including lignocellulosic biomass feedstock, can be converted to methanol, first by producing synthesis gas via oxygen-gasification followed by a shift reaction, acid gas removal and methanol synthesis.

There are three major processes which are utilized to synthesize methanol from synthesis gas. They are the LURGI, ICI and CHEM SYSTEMS processes. The LURGI and ICI processes are examples of low-pressure methanol synthesis while the CHEM SYSTEMS process is a high-pressure process.

The LURGI and ICI processes utilize a highly reactive and selective, non-regenerative catalyst in a tubular and quench type reactor, respectively. The more active and selective catalyst permits a lower pressure and temperature synthesis process.

Both LURGI's and ICI's processes have met with success

utilizing coal or naphtha derived synthesis gas. However, neither process has been successfully demonstrated both technically or economically at the industrial level.

LURGI's success is due largely to its "iso-thermal" steam recovery type tubular reactor which permits a high process efficiency. ICI has countered with various designs involving improved heat recovery from the methanol loop.

The Chem Systems's synthesis is a high-pressure process utilizing a regenerative catalyst. Chem Systems claims to be able to achieve a somewhat higher efficiency than LURGI and ICI's processes, however the Chem Systems process has yet to be proven both technologically and economically at the industrial level.

Methanol is an attractive substitute to gasoline for automobile use, as well as a fuel for gas turbines, boilers and even to convert to gasoline via the Mobil process.

Scope

This report discusses the state-of-the-art review of the technology of producing methanol from biomass feedstock. Principal topics that have been discussed in this report are:

- * Synthesis gas production technology.
- * Equipment system for the synthesis gas production.
- * A typical mass and energy balance of the process.

- * Methanol synthesis processes.
- * Health and environmental considerations.
- * Investment and operating costs.
- * Applicability to LDCs.
- * Summary of findings and recommendations.

Background

The technology of methanol synthesis from natural gas and coal has been practiced widely. The technology of producing proper synthesis gas from coal can be used using biomass as feedstock. Recently, several studies have been completed on the production of methanol from wood. Such studies confirmed the technical and economic justifications for such industrial ventures. Brazil's large biomass resource will soon be used to produce methanol. Similar small scale plants are being designed for Canada and India.

Economics

The economic analysis yielded a required selling price for biomass derived methanol in the range of \$0.66/gal to \$1.33/gal depending upon the cost of the wood feedstock and the variation in capital costs ⁴.

The initial capital investment for such a venture is very high, with the initial investment for a 1000 ODT/day plant requiring about 100 million dollars. This may pose a problem for many LDCs. The cost of labor in most LDCs is much less than in developing countries, few dollars per day

versus \$12-\$20/hour, but labor costs does not comprise a large portion of the final product cost.

However, the profit derived from these plants makes up about 44 percent of the final product price. Since most ventures in LDCs would be government sponsored, there would be no profit factor, thus dropping the final selling price of the methanol by 44 percent and consequently making the cost of the methanol an even more attractive alternative to gasoline.

It is, therefore, recommended that the following procedures be adopted to assess the viability of the production of methanol from biomass in LDCs:

- * Survey the available renewable biomass resources of the country or specific region.
- * Conduct a full economic analysis of the proposed methanol synthesis process. Including the dependence on outside technical supervision, ability to meet high initial capital cost and strength of cheap unskilled labor force in the area.
- * Since the liquifaction process is still unproven using biomass as a feedstock, keep abreast of further developments in the field. Set up small plants, learn the problems associated with these systems and move up from there.

Conclusions

The prospect for methanol production in LDC's via biomass derived synthesis gas is contingent upon the following considerations:

- * Considerable technological and economic uncertainties exist at the industrial level using biomass derived synthesis gas as a feedstock.

- * The initial capital investment for such a venture is considerable, which may pose a problem for many LDCs.
- * Methanol processes are high technology requiring the importation of expensive high technology equipment and trained personnel.
- * LDC's must develop indigenous industrial and process technology to maintain such a process.
- * The synthesis gas used as feedstock for methanol production must be produced through oxygen gasification, for which cryogenic separation of air to produce oxygen has to be provided. This is an expensive high technology proposition.

Further, the actual use of methanol as an automotive fuel substitute or for use in power plants, still requires further investigation. The higher vapor pressure of methanol may cause start up problems in automotive engines. Methanol's Btu content is only half that of gasoline, thus requiring twice as much methanol to do the same amount of work.

Thus, one cannot recommend the use of biomass as a feedstock for methanol production in LDCs at this time. However, the potential for the use of methanol as a fuel substitute or supplement is great, and one should stay abreast of recent advances in the field.

III. OBJECTIVE AND SCOPE OF STUDY

The broad objective of this report is to review the state-of-the-art of methanol production from biomass feedstocks via direct gasification and methanol synthesis processes.

The scope of the work is to:

- * Conduct a literature search on the state-of-the-art of methanol processes.
- * Review the literature search abstracts. Select and procure appropriate documents for the subject.
- * Review, including flow diagrams and material balances, the LURGI, ICI and CHEM SYSTEM processes for production of methanol.
- * Discuss various gasifier designs.
- * Status of process development and its application to LDC's.
- * Provide a list of other sources in the field.

IV

BACKGROUND

A. Historical Review

As the world's energy demands increase, the search for alternative energy sources increases. The effects of these energy demands are especially felt in Lesser Developing Countries (LDC's). Because the economies of these countries are primarily agriculturally based and many have large forestry resources, the potential for biomass as a feedstock for alternate energy processes, is great.

A possible application of biomass is in the production of methanol via the direct gasification of these biomass feedstocks and wood residue. Originally methanol was produced as a key product of the charcoal industry. However, since methanol has a good heating value (56,560 Btu/gal HHV, 49,715 Btu/gal LHV)², it has a large potential as an alternate energy source, particularly, as a fuel substitute or supplement. Hence, methanol production was initiated using natural gas as a feedstock. But, as the availability of natural gas decreased the cost of production increased. Thus the cost effectiveness of methanol production decreased. As a result, many of the industrial nations shifted from natural gas to coal as their feedstock. Methanol has been produced from coal on a commercial scale throughout Europe and the U.S. for many years, using current coal gasification and high pressure methanol synthesis technology. During this period coal gasification techniques have

improved slightly. However, with the development of Imperial Chemical Industry's (ICI) low pressure (50 to 100 atm) methanol synthesis process, methanol production technology has improved greatly.

Many LDC's do not have abundant coal resources, but are rich in agricultural and silvicultural resources. A developing country with a large forestry resource could replace coal with wood as its feedstock for methanol production.

Methanol yields from wood would vary according to the type of wood used, and is estimated to be around 100-120 gal/dry ton of wood, thus achieving an estimated conversion efficiency of 48 to 50%. In the absence of any operating, large, commercial scale biomass based methanol production facilities, anywhere; the design constraints, limitations and actual economics have yet to be evaluated.

However, from the pilot plant studies conducted, it is known that methanol production facilities cannot be based on small scale industry. The technical and economic limitations of methanol plant size is estimated to be 3 to 10 million gpy.

An area of interest for methanol production is its use as a substitute or supplement to gasoline. Brazil has been using straight (95.8% w/w) ethanol and gasoline-ethanol fuel blends in their automobiles since the 1920's. Motivated

mainly by the governments interest in stabilizing the sugar industry, excess sugar and molasses was converted to alcohol in distilleries attached to sugar mills. By 1931 compulsory addition to gasoline of up to 5% alcohol was legislated.

The glamour of methanol as a powerful (higher octane compared to gasoline) fuel substitute is known in the car racing industry. Of course, it should be understood that the racing car engines burning methanol fuel are not the same design as that of commercial or passenger car engines. The lack of lubricating properties and the corrosive nature of methanol fuel, normally would shorten the engine's life, unless remedial steps are taken to compensate for the above deficiencies. The fuel injection systems and the compression ratio of the engines have to be adapted to accept the methanol fuel as a fuel substitute to gasoline.

Currently Brazil is promoting an engine which can burn straight or a rich blend of methanol. Because the vapor pressures of methanol-gasoline blends are higher than for gasoline alone, vapor lock problems can result in the fuel system. The stability of these blends is dependent upon the composition of the gasoline and the amount of water present in the methanol. Methanol technology has evolved to the point where the methanol's water content is less than one percent, as opposed to ten to twenty percent water content from older technologies. This results in a more suitable methanol component for methanol blending.

The high octane number, 106, the absence of exhaust pollutants, and superior efficiency and combustion properties, indicate that methanol itself may be more suitable as an alternative to gasoline. However, there are some disadvantages to using straight methanol. Methanol's high heat of vaporization can cause start-up problems, especially in cold weather. In addition, methanol's Btu content is only half that of gasolines, consequently requiring twice as much methanol to do the same work. Methanol's lubricating properties are not the same as gasolines, indicating redesign of the fuel pumps may be necessary, as well.

Clearly the sole use of methanol as a fuel substitute requires further investigation. In LDCs where fossil fuels are scarce and expensive, and large biomass potential exists, the use of methanol as a fuel substitute is an attractive alternative. However, since only proven technology and economically justifiable processes should be instituted in LDCs, it is prudent at this stage, to wait for the full development of a commercial size wood to methanol production plant in developed countries.

B. Literature Search

The principal resources for the literature search were the following:

- * Library research with the emphasis on the thermo-chemical conversion of biomass.
- * Personal contacts via telephone calls and personal communications to the E.P.A., D.O.E., and various research and consulting engineering firms.

C. Feed Preparation

Methanol is produced from appropriate synthesis gas. By proper oxygen gasification processing of the biomass, a medium energy synthesis gas containing an appropriate ratio of H₂ to CO (2:1) could be produced.

The feedstock preparation for producing synthesis gas will depend upon the availability and type of biomass, the gasifier design, the method of feeding the biomass to the gasifier and the available technology in the country.

DM International has stated that any biomass containing moisture up to 50% (wet weight basis) and having a size up to 6" x 6" with a maximum of 10% sawdust, could be used to produce synthesis gas. In some installations, wood logs, bagasse, chips, husks, fruit pits, cotton gins etc. have been used as feedstock. It is understood, therefore, that there is no one series of feed preparation steps that are applicable to all feedstock varieties.

For atmospheric pressure updraft gasifiers, wood logs and chunked wood can be used. For pressurized gasifiers, however, such a feed cannot easily be fed into the gasifier. For pressurized fluidized bed or fixed bed gasifiers, wood chips, hogged fuel and densified biomass (pellets) are more appropriate.

It is important that the gasifier fuel bed be designed to act as a packed bed. For a uniform packed bed gasifier,

the heat transfer from the rising hot gas coming into contact with the carbonaceous feedstock bed, promotes efficient gasification.

So the first step in the feed preparation is proper sizing of the feedstock. In developing countries where large scale automatic wood chippers or hogging equipment are not available, atmospheric pressure fixed bed or fluidized bed gasifiers will probably be used. The feed for the fixed bed gasifier could possibly be processed by manual labor. In LDC's, labor intensive projects, where large numbers of unemployed, unskilled, and cheap labor forces could be utilized, serve both the social and economic needs of the country.

Since in the oxygen gasification of biomass the moisture content of the biomass is evaporated by using oxygen, which is very expensive, it is important that the feedstock first be air or sun dried to bring the moisture content down to 15 to 20%. In many of the tropical developing countries, the moisture content of the green biomass could be lowered to 10 to 15% by splitting the wood and sun drying them.

For advanced developing countries and for large installations, mechanical whole tree chippers and hogging machines have to be employed. Rotary dryers utilizing the available waste heat from the hot synthesis gas could be used to dry the green wood feedstock. A typical scheme for utilizing the mechanical rotary dryer is shown in figure 1³.

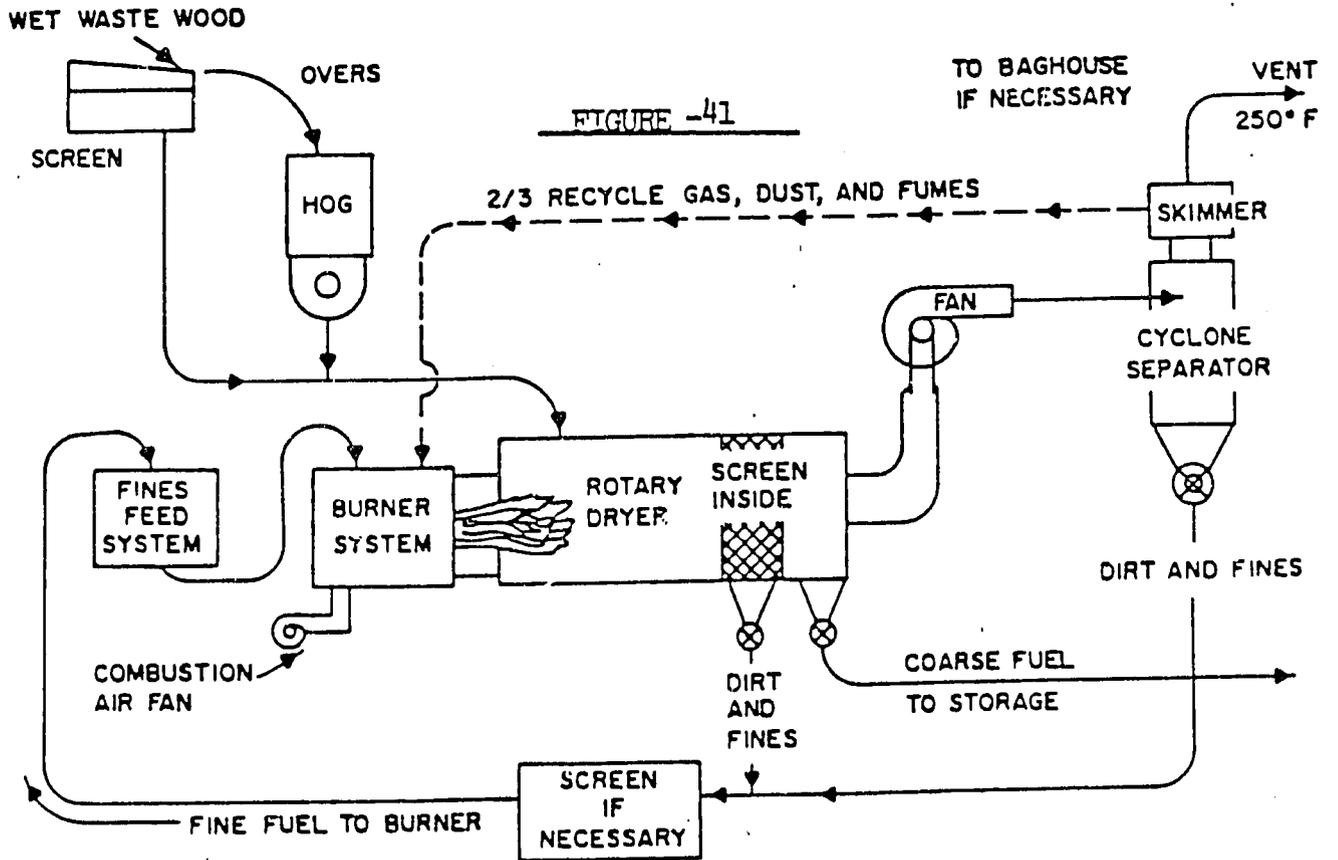


FIGURE- 1

TYPICAL ROTARY DRYER SYSTEM

Detailed discussion of the feed preparation can be found in reference 3.

A simplified scheme for densifying agricultural biomass is shown in figure 2⁷.

Pelletizing involves extrusion dies and maintenance of the dies will generally be prohibitively high for a developing country. However, pellets are an ideal feed. It packs well and can be stored conveniently for long periods of time. Moreover, pellets form excellent porous beds and therefore are an excellent gasifier feed. The pellets could be stocked in bags, in silos and even outdoors without any deterioration of its fuel quality.

Specifications for biomass pellets ideal for synthesis gas production are:

- * Heat content (average) 8,200 Btu/lb
- * Moisture (maximum) 10 %
- * ASH (maximum) 5 %
- * Density (average) 38-40 lb/cu.ft.
- * Fines (by weight) 5 %

- * Size 1" cube or
1" diameter

Although wood chips have been used more often than pellets in gasification processes, wood chips have one disadvantage compared to pellets. In a packed bed gasifier, heat transfer from the rising gas stream to the packed bed of

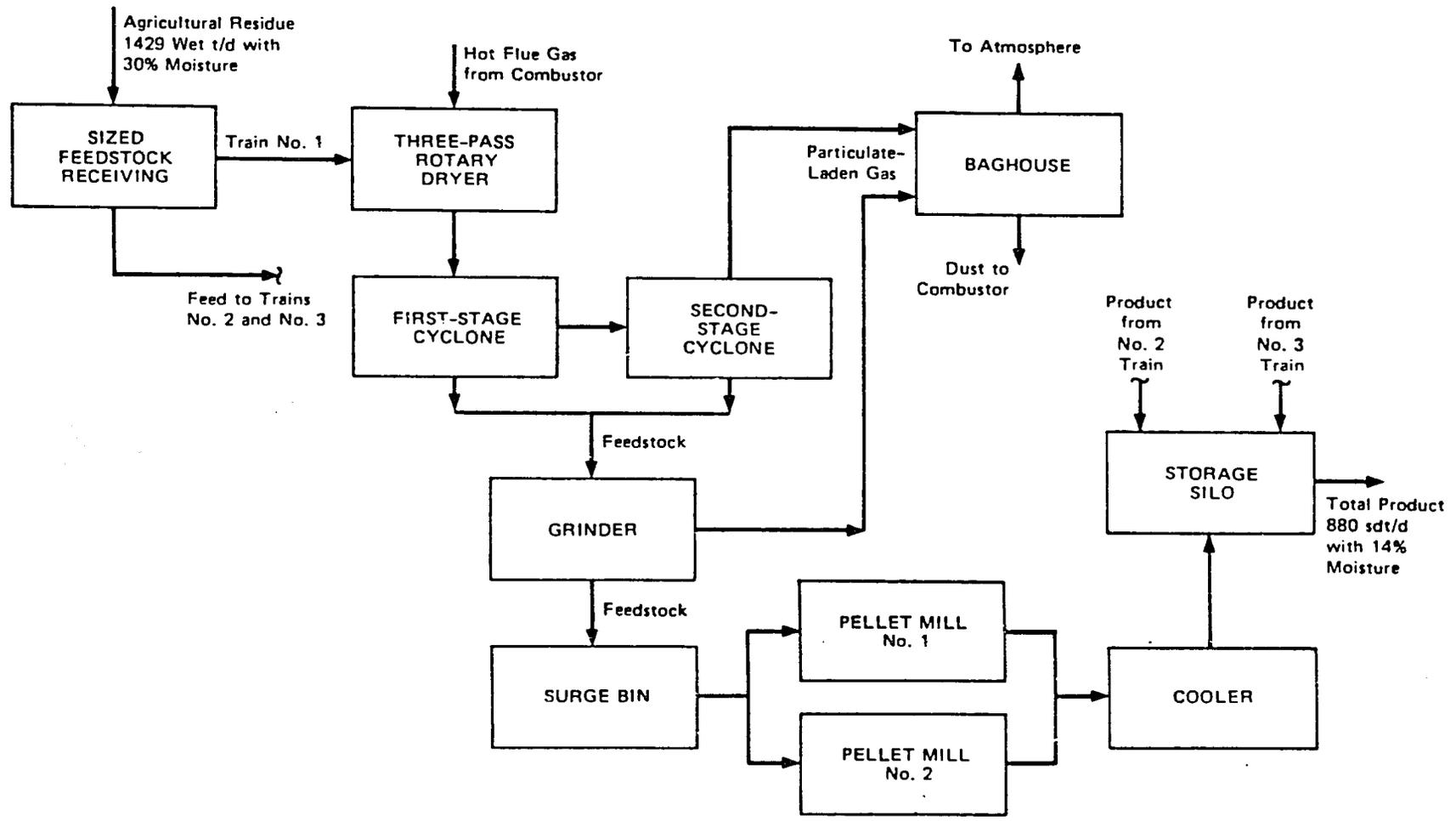


FIGURE -2 SINGLE-TRAIN RESIDUE PELLETIZING PLANT

Source: Reference -7

wood chips is diminished by the fact that each wood chip acts as an insulator, and unless the hot gas can find a way to flow in between each layer of wood chips, the gasification process could be slowed down considerably.

The preferred wood chip size for gasification (especially for pressurized units) is minus 2 inches.

To produce minus 3/2 inch size chips, first the products from the whole tree chipper are screened for + 2 inch size chips. The + 2 inch size chips are then passed to hammer mills with proper size screens and minus 2 inch chips are produced. The oversized chips are recycled to produce more minus 2 inch chips. The chips could then be sun dried or mechanical waste heat dryers could be used to bring the moisture content down to 7 to 10 %.

Another preferred biomass feedstock is hogged fuel. The hogged fuel could be composed of bark, wood, agricultural residues, and wood residues and wastes. Husks, sawdust and fruit pits etc. could serve as genuine feedstock to gasifiers. However, husk and sawdust use should be restricted to 5 to 10% (weight basis) of the total feed and should always be fed in conjunction with chunk wood, chips, hogged fuel or pellets. By doing this the carry over to the product gas is minimized.

V. PROCESS DESCRIPTION

A. Syn Gas Production

Any carbonaceous solids can be converted to synthetic gas by a partial oxidation or gasification process. The gasification of biomass could be constructed as:

1. Air blown.
2. Oxygen blown.
3. Atmospheric pressure.
4. Elevated pressure.
5. Fixed bed (moving fuel bed).
6. Fluidized bed.
7. Entrained bed.

In an air blown gasifier, the product gas contains 46% nitrogen and therefore produces what is commonly called a low-Btu gas (LBG). The principal constituents of the product gas in an air oxygen blown gasifier are H_2 , CO, N_2 and CO_2 . The oxygen blown gasification process produces a medium-Btu gas (MBG). This gas is used as a synthesis gas to make methanol.

Fixed bed gasifiers are sometimes called moving fuel bed units. They could be of updraft, downdraft or crossdraft design. Such gasifiers use bulky feedstocks like pellets, woodchips, wood chunks, corn cobs, etc.

Fluidized bed gasifiers use an inert bed over which the finely shredded biomass are fed. During operation the inert

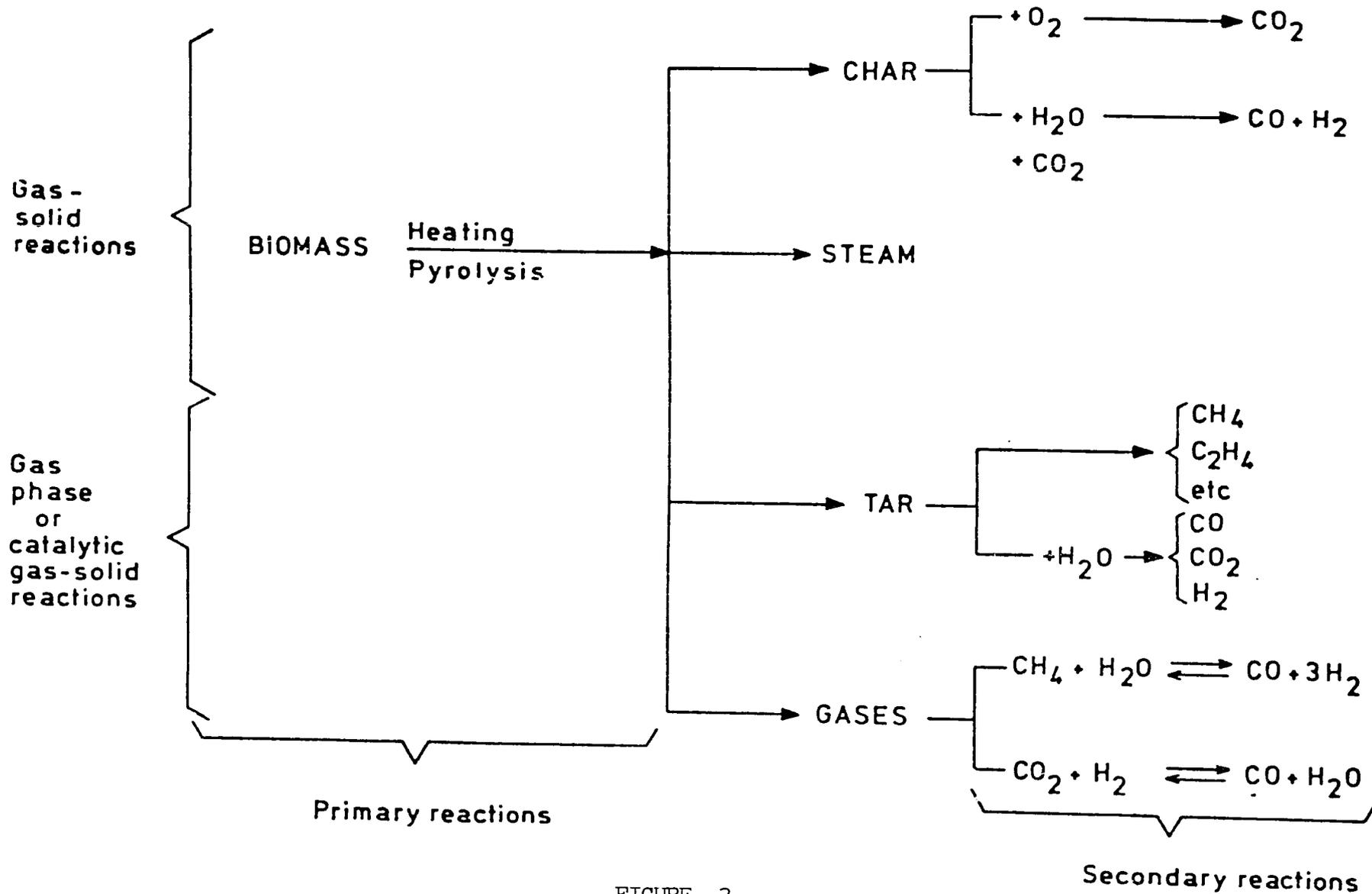
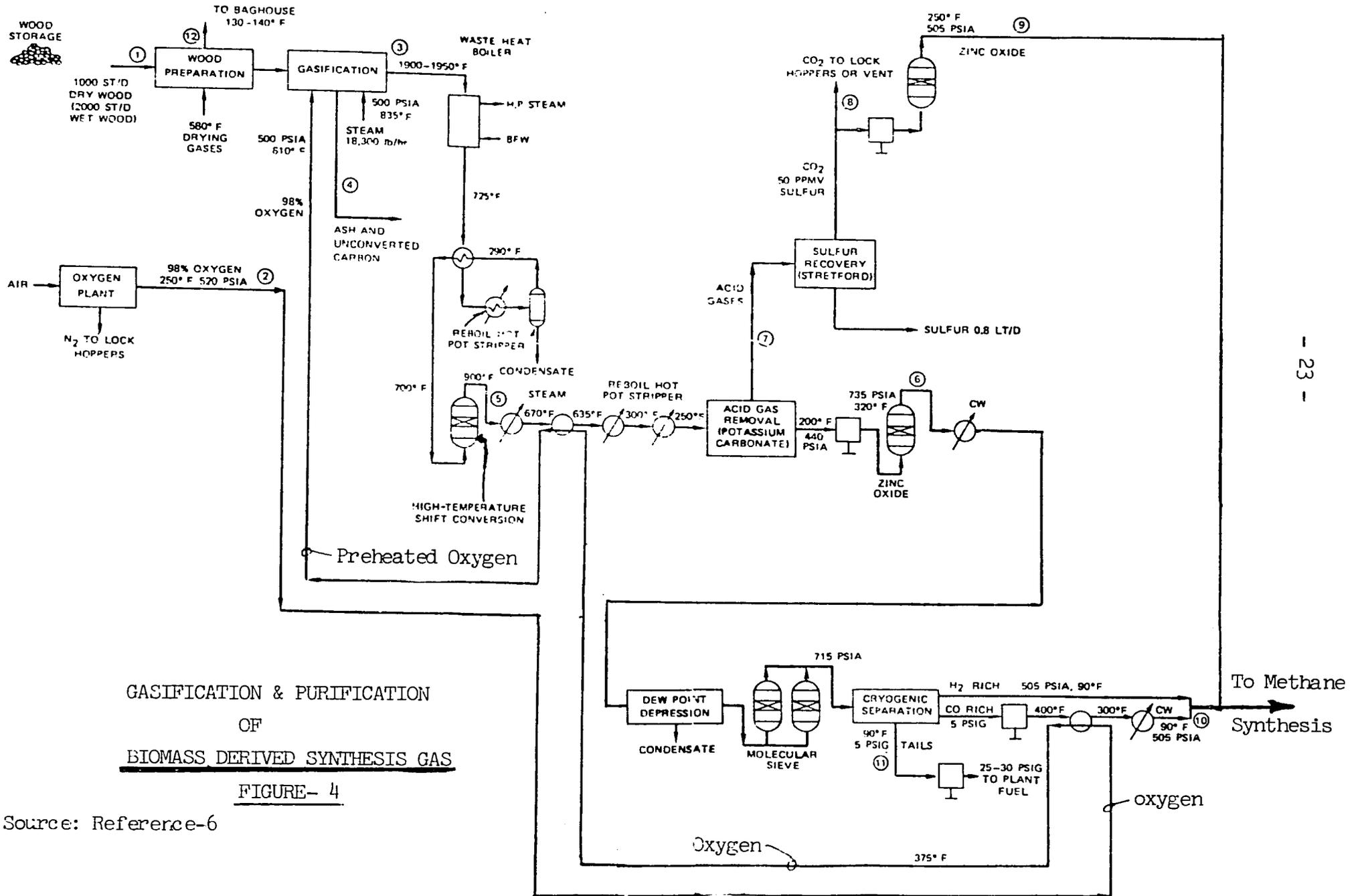


FIGURE- 3
 PRINCIPAL REACTION PATHS IN BIOMASS GASIFICATION.

Source: Reference-3



GASIFICATION & PURIFICATION
OF
BIOMASS DERIVED SYNTHESIS GAS

FIGURE- 4

Source: Reference-6

bed is fluidized and active heat transfer occurs between the biomass feedstocks and the fluidized inert bed.

The product yield from a fluidized bed is many times higher than from fixed bed units. For this reason, for a given size plant, fluidized bed is preferred. But the fixed bed unit is of simple design and is nothing but a vertical shaft furnace. For this reason, atmospheric pressure fixed bed gasifiers are widely used. But for large gasification processes, a fluidized bed reactor is considerably smaller in size and is therefore highly desirable. Similarly, for a given throughput rate, a pressurized fixed bed gasifier is much smaller in size than similar atmospheric pressure units.

The principle reaction paths followed during the gasification of biomass are presented in figure 3³. These reactions are independent of the type of gasification chosen.

A flow diagram for the direct gasification of biomass, in this case wood, is given in figure 4⁶.

In this process, wood chips are preheated to 610⁰F and fed into a 500 psia fluidized bed gasifier where it is gasified in the presence of oxygen and steam to produce a medium-Btu synthesis gas containing H₂, CO, and CO₂. The design considerations for various gasifiers will be discussed in a later section.

This medium-Btu gas leaves the gasifier at roughly

200°F. From there the gas enters the multistage cyclones (not shown in flow diagram) where the particulate contents of the gas is reduced to less than 0.025 grains/scf. These collected particulates are returned to the gasifier bed. Ash and unconverted carbon are discharged through the bottom of the gasifier and stored in lock hoppers. From the cyclones the hot product gas is cooled to 725°F in a waste heat boiler, generating high-pressure superheated steam. About 70 percent of the water content of the syngas is then removed by cooling to 290 to 300°F. Then the syngas is again reheated by waste heat reboiler effluent to 700°F. The dry heated synthesis gas is then routed to the high temperature shift converter.

The condensation step acts as a wet scrubber to remove small amounts of particulates, tars, and oils still in the gas stream. The water gas shift reaction is expressed as $H_2O + CO \rightleftharpoons H_2 + CO_2$. In addition, this reaction ensures that enough water will be removed to allow a portion of the carbon monoxide in the gas to be converted to hydrogen. No steam is added at the shift converter, because of the moisture content of the feed gases. The water-gas shift reaction takes place in the shift converter at 470 psi. The shifted gases are then cooled to only 50°F through successive cooling of gases in the waste heat boiler, O_2 heat exchange reboiler, and pot stripper. These cooled gases are then sent to an acid-gas removal system utilizing a hot potassium carbonate reactant. Here the carbon dioxide content in the

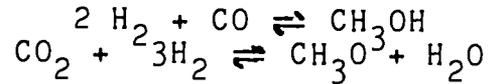
gases is reduced to 0.02 vol. percent with 95 percent H₂S removal and 70 percent CO₂ removal, assumed. The acid gases with an H₂S concentration greater than 0.2 mole percent are then sent to a Stretford unit for sulfur recovery. After acid-gas removal the purified syngas, at 440 psia, is compressed adiabatically to 735 psia and then passed through a zinc-oxide bed for further sulfur removal. The heat of compression is used to allow reasonable space velocities to be utilized in the zinc-oxide desulfurization step. Next the desulfated syngas (<1/4 grain per scf) undergoes a dew point depression step. That is, it undergoes dehydration or absorption chilling to remove most of its moisture content. This must be done to ensure reasonable sizes for the cold box feed preparation step (molecular sieves) to be used. The molecular sieve bed removes the last traces of water and CO₂ in the gas before undergoing the cryogenic separation step. The cryogenic separation step separates the syngas into three streams ⁶.

- * A high pressure, hydrogen rich stream containing approximately 95 percent hydrogen.
- * A low pressure CO-rich stream composed of approximately 93 percent N and CO.
- * A low pressure tail stream, containing the bulk of the methane in the syngas stream.

The low pressure tail stream is compressed and sent to meet the plant's fuel needs. The CO-rich stream is then compressed to 505 psia, cooled to 90°F and combined with the high pressure hydrogen stream to form an H₂ /CO mol ratio of 2:1. It also combines with a small amount of CO₂ from the

Stretford desulfating unit, to meet the methanol synthesis requirements.

The methanol synthesis reaction is represented as:



At this point, the current technologies vary as to how to produce the methanol, although the actual synthesis reaction is the same.

Equipment System

The equipment system necessary for the production of synthetic gas will depend mainly upon the type of gasifier, and the feedstock variety (size, shape, etc.). The typical equipment system for a pressurized oxygen blown gasifier using wood chips and/or biomass pellets as feedstock is described below.

1. Feedstock receiving, preparation, storage, and retrieval systems.
2. Handling and conveying feedstock to the gasifier feed mechanism system.
3. Oxygen plant or oxygen storage tank facility.
4. Gasifier with appropriate feeding and ash handling equipment system.
5. Auxiliary gas/oil burner system.
6. Gas compressor.
7. Instrumentation.
8. Hot gas cleaning and cooling system.

For properly sized wood chips or pellets, silo or domed storage facility is quite adequate. Although live bottom,

fully automated and variable speed drive retrieval facility for engineered storage bins would be used in the industrial countries. Much of the same chores could be accomplished in developing countries by a careful use of manpower. Abrasive backed or cleat mounted belt conveyors could be used to transport the chips from the ground level storage space to the top of the gasifier feed system.

For atmospheric pressure gasifiers equipped with single belt feeder mechanisms, even manual feeding of the feedstock has been advocated by some engineers. Fibrous materials like hogged fuel, wood wastes, and agricultural residues, normally tend to bridge or pack in bulk storage bins and require mechanical unloader systems. For granular or free flowing materials like pellets and wood chips, such retrieval systems may not be necessary. For small sized (less than 1" size) feed stocks, pneumatic handling in loading storage bin, and feeding to the gasifier feeder system has been practiced. For such free flowing materials, the feedstock could be received in a covered tipping floor and the bob-cat (tractor with a bucket) operator can feed material directly to a pit located conveyor. In developing countries, a pickup truck with a plough mounted in the front, can do this job, or even manpower equipped with shovels has been used in loading/unloading and feeding systems.

Synthesis gas is generally produced in oxygen blown gasifiers. Only for large gasification process plants,

installation of a cryogenic oxygen plant could be justified. Otherwise, oxygen gas could be purchased from local oxygen gas producing companies and stored on the job site. It is preferable that the oxygen gas is stored on-site at elevated pressure so that during feeding of the gas to the gasifier no further gas will be required. Oxygen gas is generally stored on cryogenic containers. The containers are normally supplied on a rental basis by the gas producing company.

Gasifier design may be fixed bed or fluidized bed. Gasifiers can be operated at atmospheric pressure or at elevated pressure. For large installations, fluidized bed or high pressure fixed bed gasifiers are preferred.

Design basis for pressurized gasifier feeding systems may involve double bell, locked hopper, pressurized diminishing screw or ramming devices. Specific selection of the feeding device will depend upon the operating pressure of the gasifier, the variety and particle size of the biomass material and the size of the gasifier. For each of the above feeding devices, the hopper has to be pressurized above the operating pressure level of the gasifier. A portion of the synthesis gas produced from the gasifier, may be cooled, cleaned and compressed to be used in the feeding mechanism.

With the success of many of the pressurized coal gasifier operations, the feeding system design has been found to be technologically attainable. Specific detailed design of

a pressurized feeder system is beyond the scope of this study. Double bell feeding system has been used for years to moderately pressurize blast furnaces. Similar designs may also be adopted for operating gasifiers operating at 2 to 3 atmospheres pressures.

Ash trapping and ash removal system design for pressurized gasifier units is more complicated. Unless careful design is incorporated in the ash trapping device, loss of valuable carbons may occur. However, as the ash content of the biomass is very low, continuous ash dumping and ash removal system may not be required. For atmospheric pressure gasifiers, ash removal is simple and can be accomplished by hydraulic or air operated dump grate system. Such a grate is designed like a collapsing shutter. That is, closing and opening of the shutter could be achieved by a centrally mounted drive rod that is activated pneumatically or hydraulically. Even hand crank type dump grates could be designed for batch dumping of ashes from small gasifiers.

Oxygen to the gasifier is generally injected through a water cooled tuyere nozzle. The tuyere nozzle could be located at various elevations evenly distributed at a given elevation around the gasifier shell, and the supply of oxygen to each of the tuyere could be maintained from a bustle pipe mounted around the gasifier. For granular or free flowing feedstock, the tuyere nozzle could be installed pro-

truding 4 to 6" inside the gasifier shell. For stringy and fibrous materials the nozzle tips should be buried flush with the refractory lining and the high velocity oxygen nozzle has to be designed to obtain the desired penetration into the fuel bed.

In most of the oxygen blown gasifiers, steam has to be injected to achieve the water-gas shift reaction and to cool the bed temperature. Steam could be generated in a waste heat boiler. The synthesis gas is discharged from the gasifier at 1600 to 1800^oF. This gas has to be cooled before effective cleaning of the gas could be made. Waste heat boilers, therefore serve the dual purpose of cooling the gas from 1600 to 1800^oF to 300 to 500^oF, and thereby generate superheated high pressure steam. For downdraft fixed bed gasifiers, using feedstock containing high or moderately high moisture, the use of steam to achieve the water-gas shift reaction may not be required. The free moisture of the feedstock is adequate to supply the necessary moisture for the water gas reaction.

Auxiliary gas/oil burners are used in the start-up process of the gasifier. After long shut down or after major repair of the refractory, the auxiliary burners are used to gradually bring the temperature up to the operating temperature level (50 to 100^oF/hr). The auxiliary burners are also used to initiate first combustion of the feed inside the gasifier. The burners are to be equipped with complete

combustion safe-guard devices (UV detectors) and air to fuel ratio control.

For pressurized feed systems, the lock-hopper containing feed material has to be pressurized above the gasifier operating pressure. One method of pressurizing the lock-hopper is to use the cooled synthesis gas from the waste heat boiler exhaust, clean it by passing it through a cyclone or electrostatic precipitator at the lock-hopper and then supplying the cool, clean gas, properly compressed to the locked hopper. Inert gases like N_2 and oxygen cannot be used in the pressurization process. It will dilute the product synthesis gas composition.

Gasification process requires elaborate instrumentation and controls to sense pressure, temperature, feed level, and gas composition.

Gas cleaning and gas cooling can be accomplished by numerous methods. In the case where first stage cooling of the gas is accomplished through waste heat boiler, the cooled gas could first be cleaned by a multi stage cyclone followed by a scrubber. Scrubbing the gas will allow the tars and fine particle ashes to be removed. Scrubbing may help to remove and acidic condensable vapors present in the gas. The wash water, however, will need to be treated for continued use and recycling. Electrostatic precipitation or bag houses can clean only dry solid particulates. Bag houses with fiberglass bags can handle gas at 500-600°F.

Dry electrostatic precipitators can handle gas in the same range. Wet electrostatic precipitators can remove both solid and condensable vapors from the gas stream. Normally, electrostatic precipitator is high in initial capital costs, but low in maintenance cost. Bag houses are low in initial cost but high in maintenance cost and a scrubber is low in initial cost, but the cost of water and water treatment and maintenance of the nozzles and other equipment systems make the maintenance cost very high.

Mass Balance

A typical flow diagram for methanol synthesis is shown in figure 5⁴. It is based on a 100 Dry tons per day wood feed rate. Fuel gas recovered from the process is used in the utility plant and excess fuel gas is exported as product. A typical mass and energy balance is given for the Chem Systems Methanol Synthesis Process in table 1 and table 2⁶.

It can be seen from this total energy balance that Chem Systems projects a process efficiency of 57 percent. This is somewhat higher than Lurgi's, ICI's or most other low pressure synthesis processes whose process efficiency is between 42% to 48%. However, as no industrial scale Chem System methanol plant is operating anywhere, the achievable conversion efficiency of Chem System methanol system has yet to be demonstrated.

FIGURE- 5

BLOCK FLOW DIAGRAM OF MAJOR PROCESS UNIT(METHANOL SYNTHESIS)

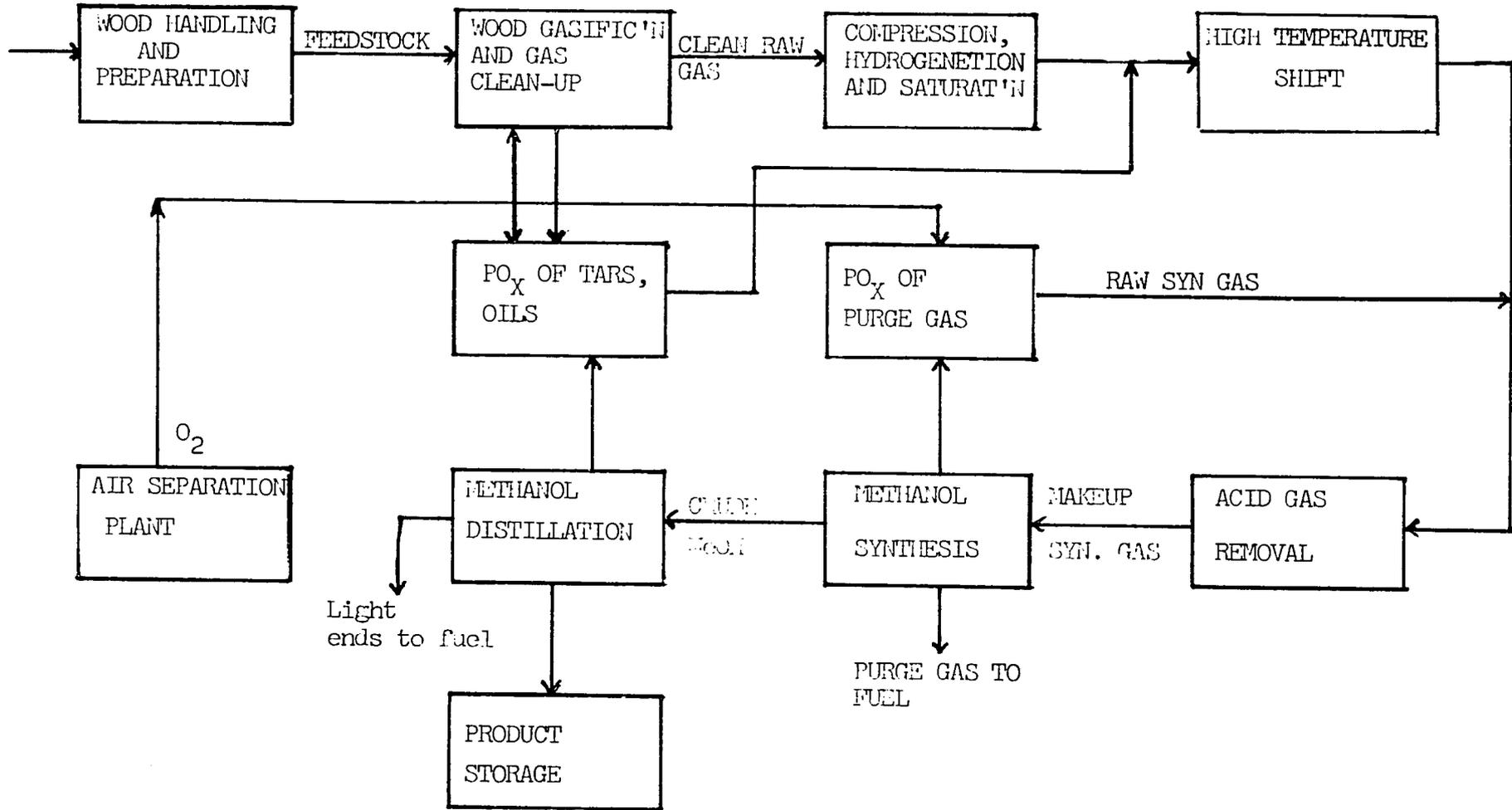


Table-1

PRODUCTION OF METHANOL FROM WOOD BY DIRECT GASIFICATION AND
CHEM SYSTEMS SYNTHESIS -- OVERALL MATERIAL BALANCE
(Basis: 1,000 Dry Short Tons Per Day Wood Feed Rate)

Source: Reference -6	<u>Thousands of Pounds Per Hour</u>
Input	
Wet wood	166.7
Water	775.5
Oxygen	42.0
Combustion and dryer air	<u>331.3</u>
Total	1,315.5
Output	
Methanol	47.8
Ash and unburned carbon	2.1
Dryer stack	373.6
CO ₂ to stack	83.4
Treated wastewater	323.1
Evaporation losses	485.4
Sulfur	<u>0.1</u>
Total	1,315.5

Table-2

PRODUCTION OF METHANOL FROM WOOD BY DIRECT GASIFICATION AND
CHEM SYSTEMS SYNTHESIS -- OVERALL ENERGY BALANCE
(Basis: 1,000 Dry Short Tons Per Day Wood Feed Rate)

Source:Reference-6	<u>Millions of Btu Per Hour</u>	<u>Percent</u>
Input		
Wet wood	796.7	99.1%
Electricity	<u>7.5</u>	<u>0.9</u>
Total	804.2	100.0%
Output		
Methanol	458.8	57.1
Heat rejected to cooling	281.2	35.0
Stack	44.4	5.5
Ash and unconverted carbon	7.1	0.9
Insulation losses	8.0	1.0
Miscellaneous losses*	<u>4.7</u>	<u>0.5</u>
Total	804.2	100.0%

* Because of mechanical inefficiencies.

B. Methanol Synthesis Processes

Many companies offer methanol synthesis processes: Vulcan- Cincinnati, ICI, Lurgi, Mitsubishi and Selas-Polimex are examples of a few⁸. In recent years ICI and Lurgi have dominated most of the contract awards. Recent methanol production has been based on a copper-catalyst in a "so called" low pressure methanol process.

The ICI process utilizes a quench type reactor while the Lurgi process uses a tubular reactor (analogous to a heat exchanger) with boiling water in the jacket and catalyst in the tubes. Lurgi's success is due largely to this "iso-thermal" steam recovery type of reactor which allows for a high process efficiency. Naturally, licensees of ICI have countered with various designs involving improved heat recovery from the methanol loop.

Methanol production is a highly competitive field with a number of proven processes as described earlier. A promising new process, supported by E.P.R.I., is Chem Systems' Liquid Phase Methanol Synthesis. By utilizing an inert liquid to absorb the heat of reaction they have been able to reduce the gas recycle substantially.

The Chem Systems' synthesis does show potential for a somewhat higher thermal efficiency and lower capital cost than the ICI or Lurgi system. It should be noted, however, that the Chem Systems' process has yet to be proven, both

technically and economically, at the industrial level. Hence, its applicability to LDC's cannot be recommended at this stage.

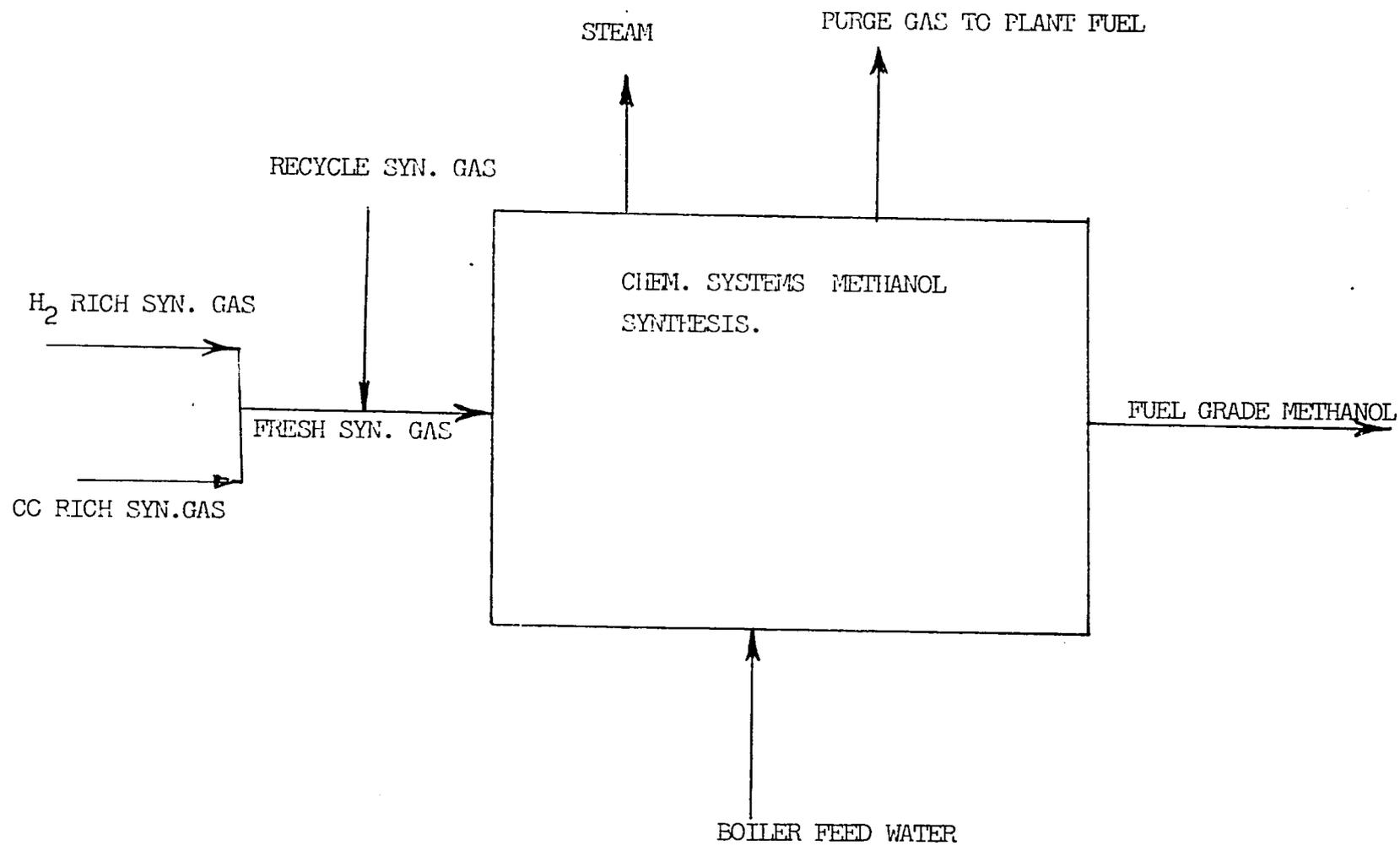
The ensuing sections will describe the following synthesis processes in detail:

- * CHEM SYSTEMS SYNTHESIS
- * ICI SYNTHESIS
- * LURGI SYNTHESIS

A. Chem Systems Synthesis

A promising new high pressure methanol synthesis process has been designed by Chem Systems. A schematic flow diagram is shown in figure 6⁶. In this process, fresh syngas is mixed with recycled syngas. The optimum recycled syngas to fresh syngas ratio, entering the methanol synthesis reactor is 5 to 1. The mixture is then passed upwards through an expanded catalyst bed which is fluidized by an inert, non-miscible hydrocarbon liquid. This works as a heat sink, absorbing the heat generated by the methanol synthesis. The heated liquid is utilized to generate steam. This is accomplished by continuously circulating the liquid from the top of the reactor through a boiler. Steam is generated by feeding water into the boiler, and is used as a means of removing heat from the reactor.

The use of the non-miscible hydrocarbon liquid allows



CHEM. SYSTEMS SYNTHESIS

FIGURE- 6

Source: Reference-6

close uniform temperature control in the reactor, allowing a higher per pass conversion of syngas to methanol.

The reactor effluent gas is then passed through a stripper column, where the inert liquid is separated from the gas. The gas is then condensed to form the product methanol and any other entrained hydrocarbon liquid. The non-condensable gases are piped off the methanol tank and recycled to the reactor, except for a small purge stream which is withdrawn to prevent the buildup of methane and nitrogen gases in the loop. These purged gases are then burned to produce high pressure steam or is used as plant fuel.

Rather than burning this purge stream, one could also utilize a power recovery turbine on the purge stream and recover additional methanol.

For the final purification steps the product methanol passes through a topping column, where light gases are removed and utilized as plant fuel, and then is passed through a refining column to remove any remaining water and impurities, yielding a fuel grade methanol.

The properties of the Chem Systems methanol fuel are given in table 3⁶.

The fuel gas from the cryogenic tail stream and the purge stream of the methanol loop could be burned to produce high pressure steam. The flue gas resulting from the

Table 3

PROPERTIES OF CHEM SYSTEMS METHANOL FUEL

	<u>Weight Percent</u>	<u>Mol Percent</u>
Methanol	95.4	94.48
Ethanol	1.0	1.16
Isopropanol	1.0	
Higher alcohols	0.1	
Water	<u>2.5</u>	<u>4.36</u>
Total	100.0	100.00
Higher heating value, Btu/lb	9,610	
Btu/gal	63,930	

Source: Reference -6

combustion process is mixed with air to form a 700°F stream which can be used for wood drying. If additional synthesis gas production is desired, the fuel gas can be redirected to a steam-methane reformer. This, however, would necessitate the use of another source of hot gases to dry the wood.

In addition Chem Systems has suggested that this process may be more economically feasible operated at 1100psi rather than 500psi. A comparison of operation at the two pressures is given in table 4⁸.

B. ICI Synthesis

ICI has developed a copper based methanol synthesis catalyst which is more active and selective than the conventional zinc-chrome variety. The greater activity of the catalyst permits a lower pressure and temperature synthesis process.

Methanol plants using the ICI low pressure synthesis process normally consist of:

- (a) A synthesis gas plant
- (b) A low pressure ICI methanol synthesis plant
- (c) A distillation plant.

The low pressure process, originally introduced in 1966 by Imperial Chemical Industries (ICI), represented a major breakthrough in methanol synthesis. ICI discovered that it

TABLE 4

COMPARISON OF 1100 PSI AND 500 PSI CHEM SYSTEMS METHANOL SYNTHESIS

Source: Reference -8

	<u>Chem Systems 1100 psi Synthesis</u>	<u>Chem Systems 500 psi Synthesis</u>
Recovery as a percentage of the thermal value of feed gas to loop as:		
Methanol	81.5	80.8
Purge Gas	<u>4.2</u>	<u>5.1</u>
	<u>85.7</u>	<u>85.9</u>
Waste Heat Boiler	11.0	10.9
Boiler Feedwater	<u>1.8</u>	<u>1.2</u>
Total	98.5	98.0
Loss to Cooler	<u>1.6</u>	<u>2.1</u>
	100.1	100.1
Capital Cost for Nominal 1300 TPD loop	9.0	15.0
Feed Gas Compressor	<u>1.7</u>	<u>-</u>
Total	10.7 MM \$	15.0 MM \$
Power Consumption		
Make-up Compressor	6,150	-
Recycle Compressor	510	2,020
Oil Pump	<u>440</u>	<u>990</u>
	7,100 HP	3,010 HP

is possible to achieve high methanol yields by utilizing low operating pressures (50 to 100 atm) and a fixed bed of copper-zinc-chromium catalyst. As a result, large numbers of methanol plants today are operating on ICI's low pressure synthesis process design.

The catalyst's high selectivity, produces a 99.85 percent pure methanol product. This subsequently reduced purification costs. The catalyst is, however, very sensitive to sulfur poisoning. Thus the H_2S concentration of the feed must be limited to 0.5ppm to maintain catalyst activity. However, unlike the high pressure process catalyst, the low pressure catalyst cannot be regenerated. Catalyst life operating in the pressure range of 50 to 60 atm is between 3 to 4 years, and at 100 atm the longest life achieved is 2-1/2 years⁷. A flow diagram of the ICI process is given in figure 7⁸. After direct gasification the resulting syngas is compressed to about 50 atm and then passed through an absorption sequence to remove H_2S or any other sulfur compounds. The syngas is then sent to a series of guard chambers where any unsaturated compounds are hydrogenated, and any remaining H_2S and chlorine compounds, which inhibit catalyst activity, are removed.

Next, CO and steam from the syngas are converted to CO_2 and hydrogen in a water-gas shift reactor, utilizing an iron-oxide catalyst. This adjusts the hydrogen to carbon monoxide ratio to that desired for methanol synthesis. This

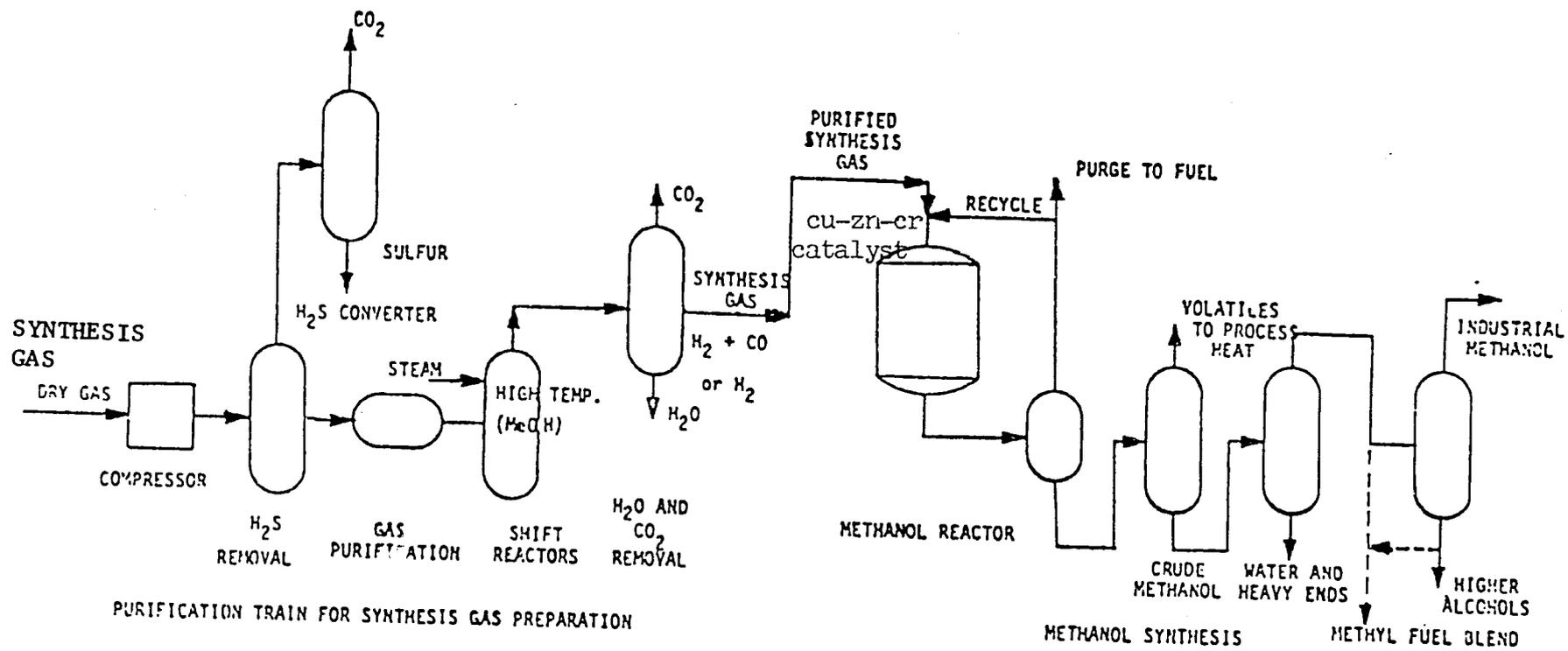


Figure--7 Low pressure methanol process (based on ICI process). (158)

Source: Reference-8

reaction takes place in a temperature range of 380-510°C (650-850)°F.

After this reaction, excess CO₂ is again removed in an effort to decrease the load on the methanol reactor and other downstream equipment. The purified syngas is reacted in a quench reactor, over a copper-zinc-chromium catalyst at 250°C (480°F), at a pressure of 50 atm, to form methanol. This product methanol is then purified in a devolatilization column and dewatering column.

If the methanol is to be used strictly as a fuel, no further treatment is necessary since any higher alcohols present in the product could only increase its Btu content. However, if a pure or chemical grade methanol is desired, the methanol must be further distilled to separate it from the heavier and higher alcohols.

The advantages of the ICI low pressure process are:⁹

- * Reduced by-product formation resulting in lower feedstock consumptions per ton of methanol.
- * Reduced compression costs due to lower operating pressure.
- * The ability to use steam driven rotary compressors on small plants.
- * Efficient heat recovery from the synthesis process.
- * The avoidance of CO₂ addition in natural gas based plants without incurring large financial penalties.

- * Lower capital costs as a result of using centrifugal compressors, simplicity in design and low pressure equipment.
- * Suitable for large and small plants.
- * Short commissioning period.
- * Proved in wide practical service.

C. Lurgi Synthesis

Since the advent of the ICI process there have been many variations on the same low pressure synthesis principle. One of the most successful of these variations was developed by Lurgi engineers.

At the heart of the Lurgi process is a tubular reactor (figure 8¹⁰). It is a vertical reactor equipped with long carbon steel tubes similar to a shell and tube heat exchanger. These tubes are closed at their lower ends by a hinged grid with a screen containing a catalyst. The void around the tubes are filled with boiling water. This affords a nearly uniform catalyst temperature over the reactor cross section and over the length of the tubes.

Lurgi uses a copper catalyst rather than ICI's copper-zinc-chromium catalyst. In order to maximize the catalyst life, a constant catalyst temperature must be obtained. In addition the temperature profile of the tubular reactor drops towards the outlet thus contributing to a better equilibrium while each stage of the quench type reactor has an increasing temperature profile.

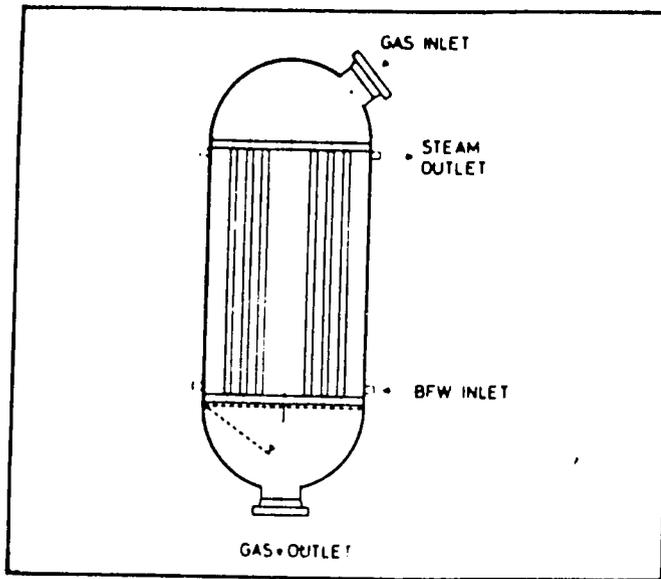


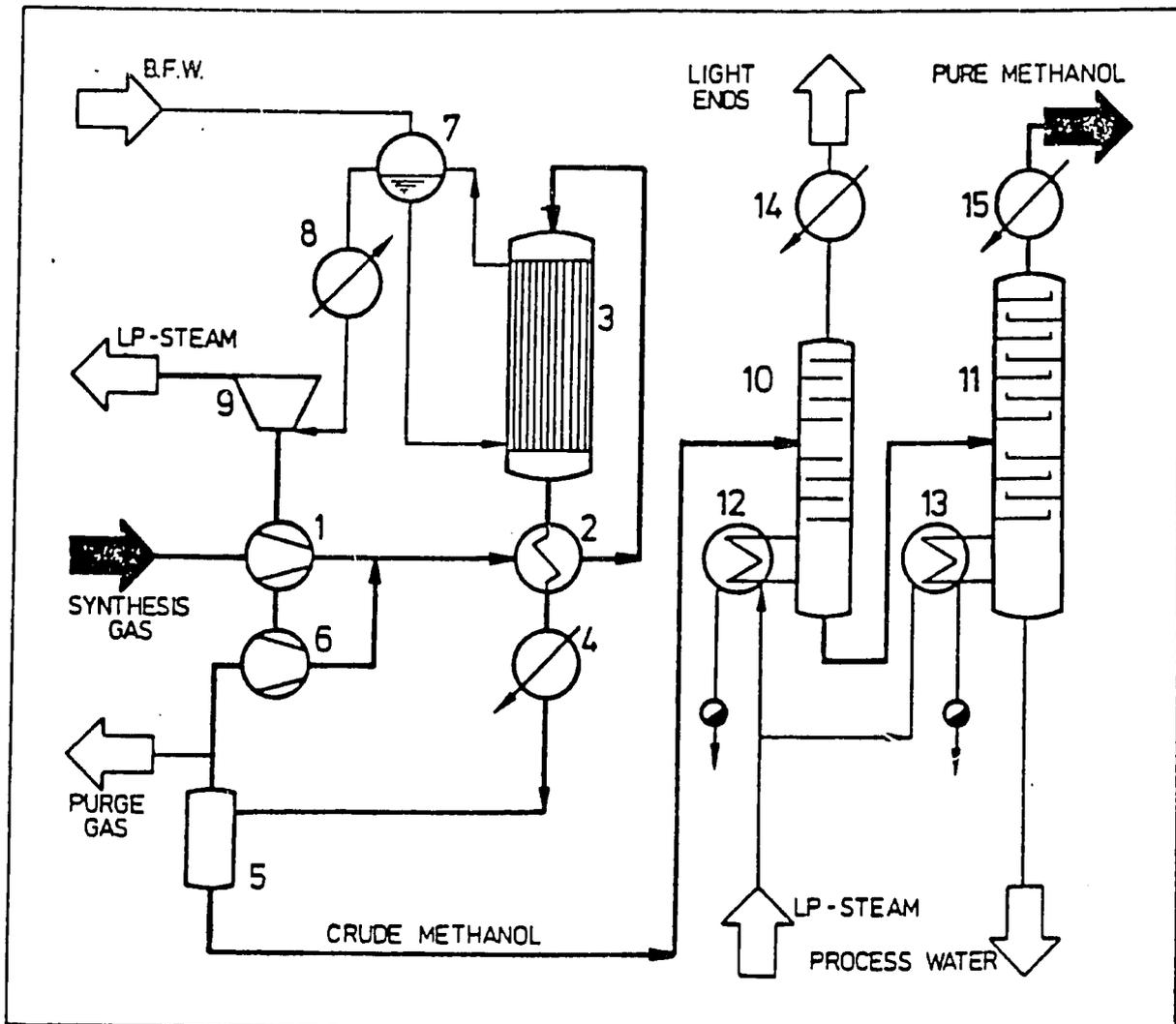
FIGURE-8

Lurgi-developed methanol reactor

Based on a design worked out for Fischer-Tropsch synthesis, this reactor is similar to a shell-and-tube heat exchanger

III. DESCRIPTION OF PROCESS

FIGURE-9



Another major advantage of the tubular reactor is that nearly all of the reaction heat can be utilized to produce high pressure steam at constant temperature conditions. In the quench type reactor this reaction heat is used mainly to raise the quench gas to reaction temperature. In addition, steam generation from the waste heat reactor exit gas can only occur at falling exit gas temperatures. This limits the maximum steam pressure to only 10 atm¹⁰.

The actual Lurgi low pressure synthesis loop does not vary very much from other low pressure processes. There are different gasifier technologies employed in the production of syngas and these will be described in detail in a later section. A flow chart of the Lurgi process is given in figure 9⁹. A numbered description of the flow chart is given below.

After direct gasification of the feedstock, the resulting syngas is compressed to synthesis pressure (from 50 to 100 atm) in a turbo-compressor (1). The compressed gas is then mixed with unreacted recycle gas which has been preheated to near reaction temperature, between 230 to 265°C, in a heat exchanger (2) and fed into the tubular synthesis reactor (3). In the catalyst filled tubes of the reactor, part of the carbon oxides reacts with the hydrogen to form methanol. The unreacted syngas which leaves the reactor contains between 4 to 6.5 percent, by volume, of methanol, depending upon the composition of the syngas. Most of the

sensible heat and part of the methanol are transferred to the reactor feed gas, cooled in the heat exchanger (2) and then cooled to ambient temperature in a cooler (4). The cooler utilizes air and water to achieve this temperature reduction. Most of the methanol is condensed here, then separated from the unreacted syngas in a separator (5), where the unreacted syngas is recycled back to the reactor by a recycle gas compressor (6). A small amount of the gas is purged from the system to prevent the buildup of inerts within the loop.

The heat generated by the methanol reaction is utilized to produce high pressure steam. The resulting steam is collected in a steam drum (7). The steam is then superheated in a superheater (8) and is used in a steam turbine (9) to drive the syngas and recycle gas compressors. The resulting turbine exhaust stream is used in methanol distillation. If pure methanol is desired, the flashed crude methanol from the separator is purified in a subsequent distillation plant.

To further distill the methanol the light-ends column (10) strips the low boiling impurities from the gas, while another column (11) removes water and other high boiling impurities. The partially purified methanol is then sent through two reboilers (12 and 13), which are heated by low pressure steam, where any remaining impurities are removed. The light-ends stream and the methanol stream are then con-

densed in condensers (14) and (15) respectively.

The properties of Lurgi's pure methanol product are given in table 5¹¹.

A comparison of other low pressure systems is given in table 6¹².

Table 5
Lurgi
Pure Methanol Quality

		Source- reference	
Methanol Content		99.9	wt.%
Specific Gravity 20°/4°		0.792	kg/l
Water Content	max.	0.02	wt.%
Boiling Interval		0.5	°C
Permanganate Test	min.	60.0	minutes
Acid Content (as Acetic Acid)	max.	0.002	wt.%
Aldehydes and keytons (as Acetone)	max.	0.001	wt.%
Volatile Iron	max.	0.01	mg/l
Ethanol		<10.0	ppm

Table -6 TYPICAL METHANOL SYNTHESIS PROCESSES IN CURRENT USE

Vendor	Catalyst	Pressure (atm)	Temperature (°C)	Reactor Type	Cooling
ICI	Cu/Zn/Al	50-100	220-290	Single fixed-bed	Multiple gas quench
Lurgi	Supported Cu	30-50	235-280	Tube in shell	Steam generation
Topsøe	Cu/Zn/Cr	50-100	220-350	Radial flow	—
Vulcan-Cincinnati	Zn/Cr	300-350	300-400	Multiple bed	Cold-shot quench, plus external gas cooling

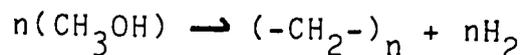
Source : Reference -12

C. Methanol Derivatives

Another potential use for methanol is as a potential feedstock for gasoline production.

1. Mobil Process

A novel process for producing high-octane gasoline from methanol and other oxygenates was recently announced by the Mobil corporation¹³. The key to this process is the discovery of a new zeolite catalyst which directly converts methanol to hydrocarbons in the boiling range of gasoline. The overall stoichiometry of the reaction is represented as:



Water is also produced as a by-product. The overall gasoline yield is about 85 weight percent of the hydrocarbons produced. The process can be operated in a fixed bed or fluidized bed mode.

However, as of this time, neither of these processes have been tested at the industrial level, although a 12,500 bbl/day plant utilizing a fixed bed mode is scheduled to be built in New Zealand in 1983-1984. A 100 bbl/day fluidized bed plant is scheduled to be built in West Germany in the late 1980's⁷.

The fact that this process is as yet unproven at the industrial level both technologically and economically,

makes this process unacceptable for consideration for applicability to LDC's.

2. China Lake Process

Another novel process for the production of gasoline from biomass and other organic materials is being developed at the Naval Weapons Center (NWC) in China Lake California. There are two basic steps to this process. First, the biomass and organic material feedstock is flash pyrolyzed via steam gasification to produce gas containing light olefinic hydrocarbons. Second, the olefins in this gas are thermally polymerized to form gasoline. This process, also, has yet to be proven, both technologically and economically, at the industrial level, thus making it unacceptable for consideration for its applicability to LDCs.

VI. HEALTH & ENVIRONMENTAL CONSIDERATIONS

Vulcan-Cincinnati has tested its proprietary "methanol fuel" in a 50 MW boiler and received encouraging results in as far as environmental effects are concerned. Test results showed that emissions of unburned hydrocarbons, sulfur oxides, and particulates are all absent. NO_x and CO concentrations in the exhaust gases were lower than what would have been produced from the burning of natural gas. EPA's tests showed that NO_x emissions were 50% to 70% lower than those released from the burning of #2 fuel gas.

The use of methanol in gas turbines operating in highly smog-ridden industrial areas, shows significant reduction of the photochemical smog producing element present in NO_x emissions².

As to the health effect of methanol, it is noted that methanol is a narcotic and intoxicant. People attempting to use methanol as an inebriant, usually experience irreversibly damaging health effects. The lowest fatal dose has been found to be 3 teaspoonfuls of 40% methanol².

Besides ingestion, both inhalation and dermal exposure to methanol may cause severe biohazards. Diminished vision, gastrointestinal disturbance and death have occurred among workers who used methanol and even in the case where total soaking of clothes and thereby exposure to skin has occurred a TLV (Threshold Limit Value) of 200 ppm (parts per million)

has been established for an 8 hour day, 40 hour work week.

(NOTE: There is no TLV for gasoline).

Methanol oxidizes to formaldehyde, the TLV of which is 2 ppm compared to 200 ppm for methanol. Estimated tolerance values for methanol are shown in table 7².

The important points on the safety and precautions that are necessary in the handling and storing of the methanol are:

- * Special means for detecting the invisible burning flame of the methanol.
- * Methanol is miscible in water at all concentrations, and gasoline is not. Therefore it is easier to extinguish a fire originating from an open spill of methanol than one from gasoline. However, as diluted alcohols have dangerous flash points, alcohol fires are not recommended to be extinguished by water.
- * Because of the miscibility of the methanol in water, in the case of a methanol spill in a body of water, it can not be sponged off as gasoline or crude oil.
- * A partially filled closed tank with methanol at ambient temperature is more susceptible to explosion than is a partially filled closed tank with

TABLE -7

ESTIMATED TOLERANCE VALUES FOR METHANOL

<u>Duration</u>	<u>Estimated Tolerance</u> <u>ppm</u>
Single but not repeated exposure	
1 Hour	1000
8 Hour	500
24 Hour	200
40 Hour*	200
168 Hour	50
30 Days	10
60 Days	5
90 Days	3
Single or repeated exposure	
1 Hour out of every 24 Hours	500
two 1 hour exposures every 24 hours	
or	
one 2 hour exposure every 24 hours	200

* based on five, 8-hour working days

Source : Reference -2

gasoline, because the vapor over the gasoline would be too rich to ignite if the concentration of gasoline in air exceeds 7.6%. This is only true for methanol when the concentration is above 36% methanol in air.

- * Both the flash point and the autoignition temperature of methanol are higher as compared to gasoline. Gasoline has -45°F as a flash point and 495°F as its autoignition temperature. These values are 52°F and 876°F respectively for methanol. This makes methanol less of a fire hazard. (NOTE: the flash point is the lowest temperature at which the vapor of a volatile combustible substance ignites momentarily when lighted by a small flame).

VII. GASIFIER DESIGN CRITERIA & AVAILABLE DESIGNS

Before any carbonaceous material can be converted to syngas, it must be partially burned or oxidized to form a crude gas containing mostly H_2 , CO and CO_2 . This oxidation can occur through the injection of air, oxygen, hydrogen or by undergoing slow or fast pyrolysis. The choice of oxidizing agent is dependent upon the desired Btu content of the resulting gas. For example, if a low-Btu gas were desired then air would be injected, resulting in a crude gas containing about 46 percent nitrogen¹⁴. This nitrogen could be separated by cryogenic means.

If a medium-Btu gas was desired, as is the case with methanol synthesis, then an oxygen/air blend or oxygen (98%) alone would be introduced to oxidize the feed material. If oxygen were used in place of air, the air must be cryogenically separated into oxygen and nitrogen, or a separate oxygen supply must be present. Hydrogen is used in liquifaction and gasification of coal and is generally used to form high-Btu gases.

In designing, building or buying a gasifier the following criteria must be considered¹²:

- * Chemical change: air, oxygen, hydrogen and slow or fast pyrolysis.
- * Method of heat and Mass contact-direct: updraft (counterflow), downdraft (co-flow), fluidized bed, direct and indirect heat sources-

- * Fuel type and form: biomass, MSW, and pellets, powder.
- * Ash type: dry ash and slagging.
- * Pressure: suction, low pressure, high pressure.

A medium-Btu syngas can be produced in a number of gasifier designs.

For further information concerning gasifier designs the reader is directed to read other USDA gasifier publications.

Modern Designs and Processes

A leading gasifier manufacturer is the Davy McKee, Inc. (DMI). DMI utilizes a modernized version of the updraft design. The major differences in the old updraft design are:¹⁷

- * Low feedstock capacity.
- * Manual feeding of feedstock.
- * Manual ash removal.
- * Outdated mechanical design.

DMI has addressed most of these deficiencies. The largest grate used ,by DMI, to date for coal processing was 13'-3" in diameter. By utilizing the same grate dimensions a gasification chamber 19 feet in diameter was designed to hold wood feedstock. This provides three times the capacity of previously available chambers and still utilized proven grate technology.

The problem of manually feeding the feedstock was overcome by utilizing a hydraulically operated lock hopper, the

preferred feedstock being 6" by 6" logs, as opposed to wood chips which require energy to produce.

Since a minimum level of ash is required to protect the grate, a minimum ash flow is necessary. Since many wood types produce little ash, it is necessary to augment the ash volume. This can be done by adding pebbles or broken fire brick to the ash.

The mechanical design of these updraft gasifiers has developed considerably since their initial use. Parts which at one time had to be cast now may be fabricated for varying capacities.

An example of a modernized single-stage fixed bed gasifier is shown in figure 10¹⁷.

This gasifier is presently being evaluated for its application to methanol production.

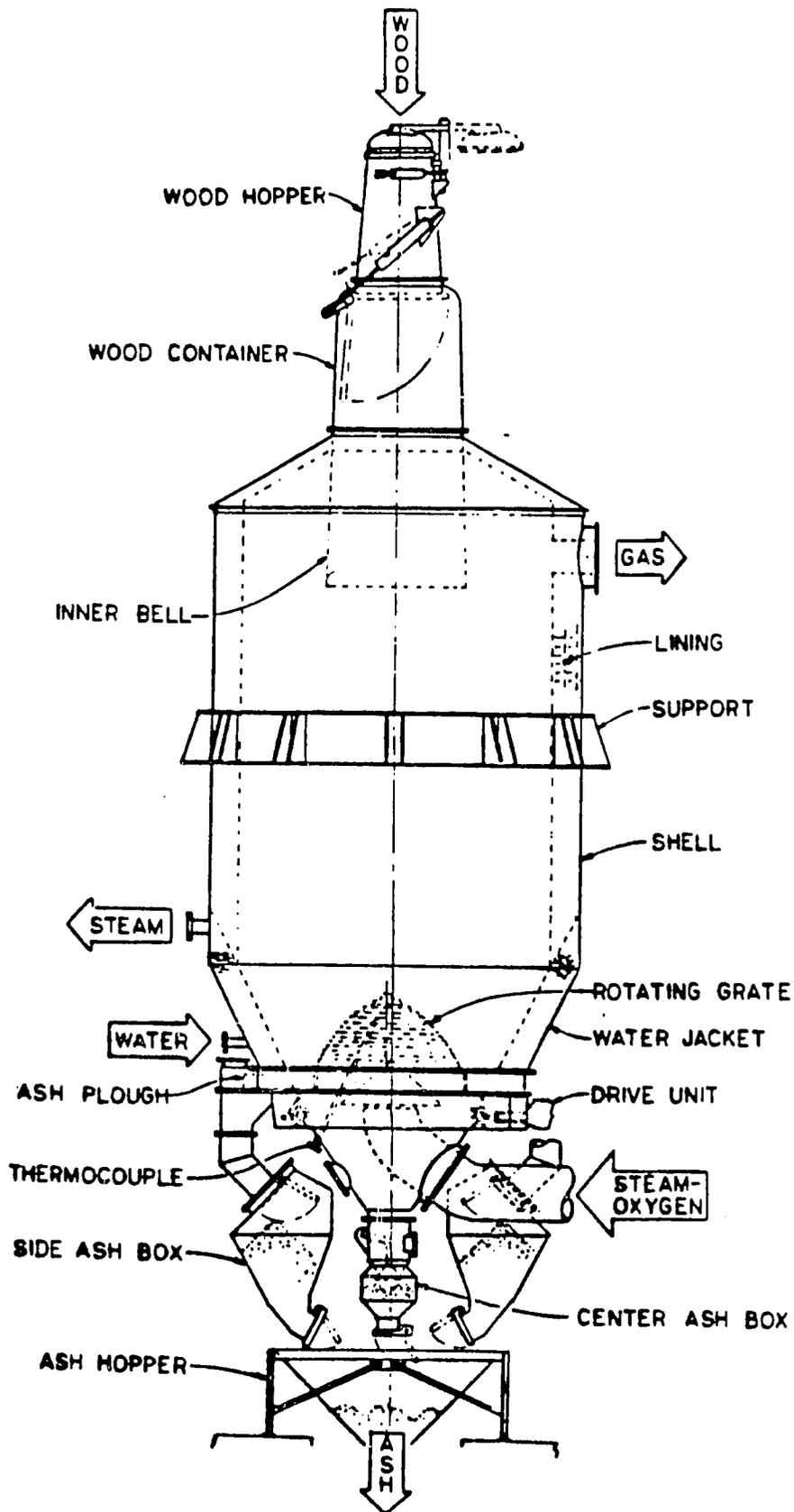


FIGURE-10
MODERNIZED WOOD GASIFIER

Two-stage Fixed Bed Gasifier

DMI has also developed a two-stage fixed bed gasifier. This two-stage gasifier is a fixed bed gasifier with two gas attacks, one above the gasification zone and one above the drying devolatilization zone (see figure 11⁹.) This type of gasifier yields a more fluid tar than a single-stage gasifier.

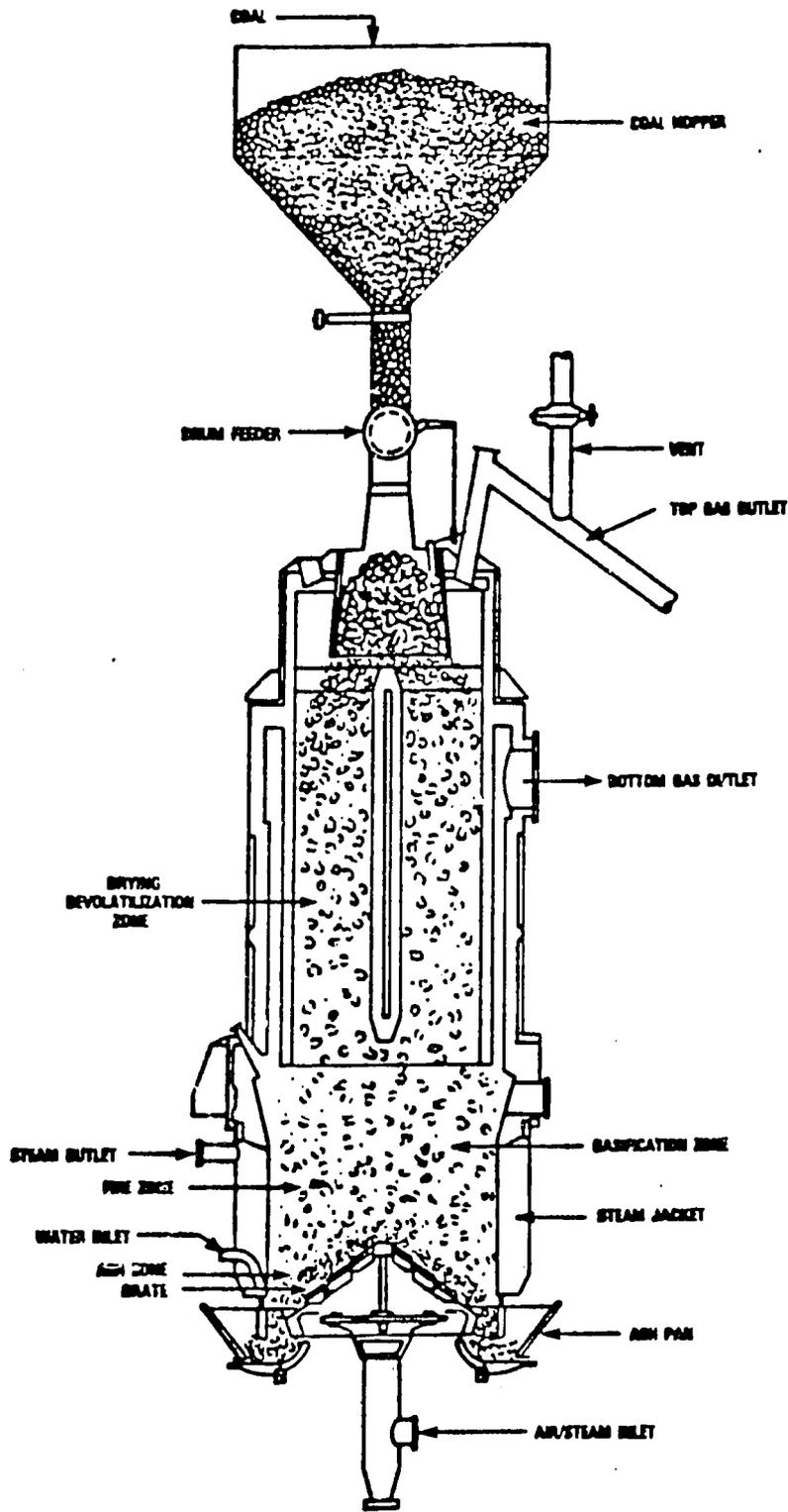
As of this time all DMI two-stage gasifiers have been air blown using coal as a feedstock. Further analytical and distillation tests must be conducted before its use with a biomass feedstock can be recommended.

Some gasifier designs are described below.

Purox

Union Carbide has developed a process for the partial-oxidation of "as-is" garbage using oxygen in an updraft (counter-current) gasifier. Although the feedstock for the Purox gasifier is garbage, it is expected to have the same crude gas composition as wood waste, since the two feedstocks are similar in composition with respect to carbon, hydrogen and oxygen.

As of this time, this design has yet to be proven at the industrial level, thus its use for LDCs cannot be recommended.



**DAVY TWO STAGE
FIXED BED GASIFIER**

FIGURE- 11

Moore-Canada

The Moore-Canada gasifier utilizes wood wastes as a feedstock to produce a low-Btu gas. Since a medium-Btu gas is required for the synthesis of methanol, this gasifier would not be recommended for methanol synthesis.

Battelle

Battelle Pacific Northwest Laboratories have designed a pilot plant moving bed gasifier which partially oxidizes municipal refuse or wood waste. However, this process produces a result similar to the Moore-Canada gasifier and hence would not be desirable for methanol synthesis.

Lurgi

The Lurgi gasifier is a tubular gasifier designed to utilize coal as a feedstock. The gasifier requires uniform particle size. Hence, if wood waste is utilized extensive preparation of the feedstock, i.e. hogging and sizing, would be required. No investigation has been done as to the Lurgi's ability to utilize wood waste.

Winkler

The Winkler gasifier is a fluidized bed gasifier, operating at near atmospheric pressure and utilizing

coal as a feedstock. This gasifier requires a feedstock particle size of less than 1/4 inch. Thus if wood waste were to be used extensive feed preparation would be required. At this time, no attempt has been made to adapt the Winkler gasifier to burn wood waste.

Koppers-Totzek

The Koppers-Totzek gasifier, utilizes a pulverized coal feedstock which is gasified at near atmospheric pressure conditions. The requirement of finely ground feedstock makes this design undesirable for adaptation to biomass, unless extensive feed preparation is employed.

These are just a few of the gasifier technologies available at this time. Although many of these processes are designed to utilize feedstocks other than biomass, these technologies presumably represent a great potential for conversion to biomass.

For more information on gasifier design the reader is directed to read references 12 and 22.

VIII. ESTIMATED INVESTMENT COST

This chapter discusses the factors which must be considered in estimating the total investment cost of a wood to methanol plant.

Total investment cost items normally consists of:

- * Land.
- * Site development.
- * Building and structure.
- * Plant facilities equipment.
- * Utilities generation.
- * Utilities distribution.
- * Engineering and supervision.
- * Royalty.
- * Contingency.
- * Working capital.

It is imperative that a large amount of background information be collected before an investment cost of a chemical plant can be estimated. Such an estimate becomes more difficult when the plant has to be designed for LDCs. The cost of labor, the level of equipment supplies available in a country, the policy of importation of foreign technology and equipment, etc. come into play.

An estimated investment cost summary for a 50 million gallon/year wood to methanol conversion plant is shown in table 8¹.

TABLE - 3
ESTIMATED INVESTMENT COST SUMMARY
(Mid 1981 U.S. DOLLARS)
(50 Million gallon/year Wood to Methanol Plant)

<u>ITEM</u>	<u>COSTS</u> <u>(\$ Million)</u>
Land Aquisition	None
Site Development	0.81
Buildings & Structures	2.12
Methanol Plant Facilities Investment	39.25
Offsite Utilities Generation	20.27
Utilities Distribution	4.88
Engineering & Supervision	8.15
Royalty	1.96
Contingency 10%	7.74
Working Capital	4.84
	<u>\$ 90.02</u>

Source: Reference-1

Table 9

Detail Breakdown of Investment Cost
Factors. (Mid 1981 U.S. Dollars) 50 Million
Gallons/Year of Wood to Methanol Plant.
Source- reference

Item	Costs (\$ Millions)
I Site Development	
Cleaning & Grading-	\$ 0.12
Paving & Roadway	0.44
Fencing	0.06
Railroad Siding	0.13
Sewer Facilities	0.06
TOTAL	\$ 0.81
II Building and Structure	
Administration-	\$ 0.58
Laboratory-	0.17
Maintenance-	0.55
Control House-	0.17
Compressor Building-	0.17
Utility Building-	0.48
TOTAL	\$ 2.12
III Plant Facilities Investment	
Wood Recieving, Handling, Processing and Storage-	\$ 4.78
Gasifier Systems & Accesories	6.36
Cooling & Scrubbing System	1.27
Organic Recovery Sustum	3.58
Primary Compression Equipment System	2.54
CO ₂ Removal Equipment	2.71
Cryogenic Seperation Equipment	5.36
Methanol Synthesis Equipment	11.65
TOTAL	\$ 39.25
IV Utilities generation	
Steam Generation Equipment-	\$ 11.45
Electric Generation	2.52
Water Treatment	1.33
Cooling Tower	2.74
Storage and Shipping	1.83
Fire Protection	0.40
TOTAL	\$ 20.27

V Utilities Distriution

Steam	\$ 1.32
Water	2.16
Electrical	1.40

TOTAL \$ 4.88

VI Engineering & Supervision \$ 8.15

VII Royalty (5% pfi) \$ 1.96

VIII Contingency 10% \$ 7.74

IX Working capital \$4.84

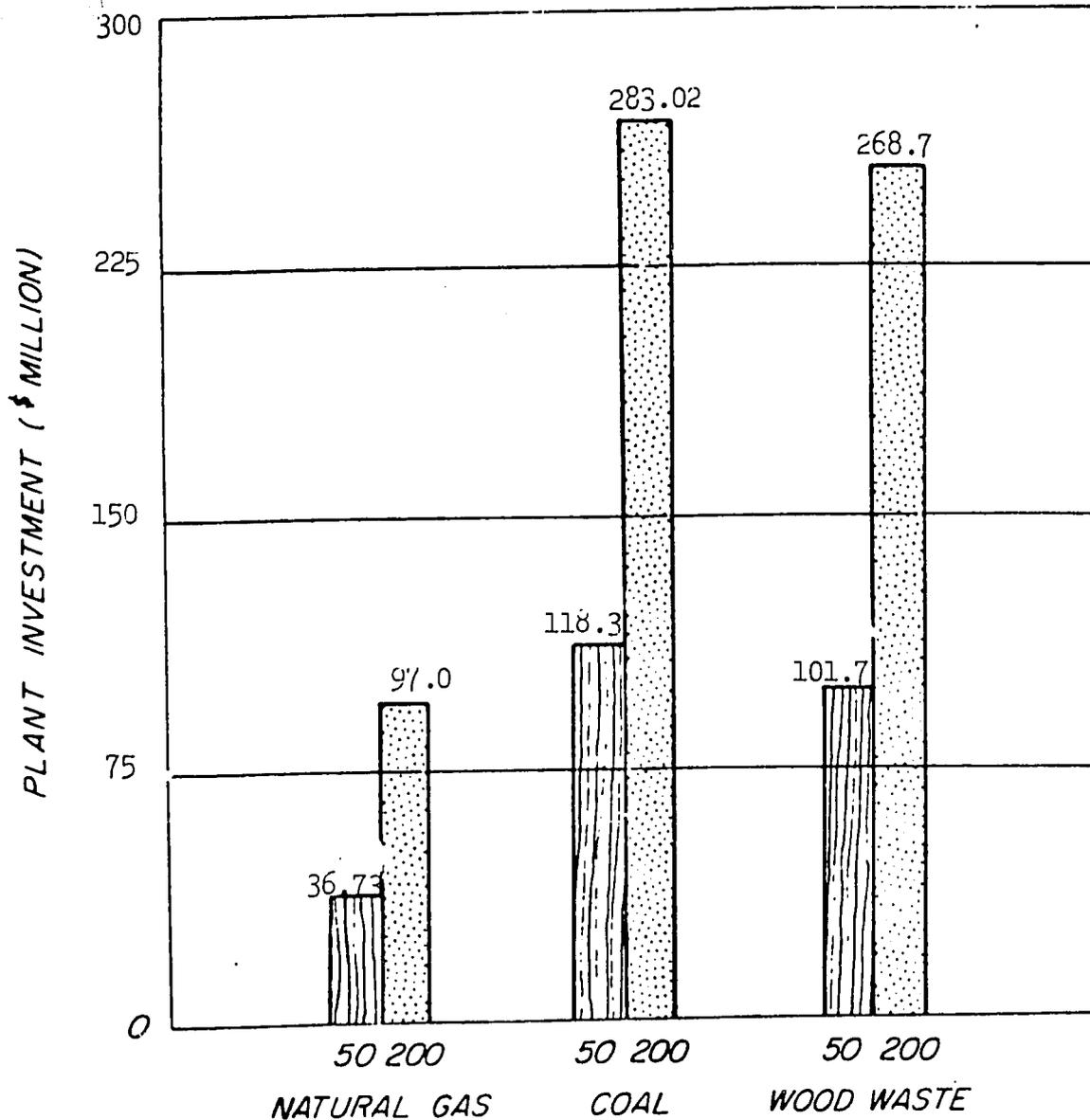


FIGURE-16

Investment Estimate

Based on 1975 costs
Includes 25% contingency
No escalation included (updated to 1981)

Figure 12 --Methanol Synthesis Plant Investment for Plants of 50 and 200 Million Gallons Per Year Facilities (Additional cost for coal vs. wood due to pressurized system, increased steam requirements, and desulfurization equipment.)

A 50 million gallon per year facility corresponds to,

$$\frac{50 \times 10^6 \text{ gallons}}{\text{year}} \times \frac{1 \text{ year}}{340 \text{ days}} \times \frac{6.61 \text{ lb}}{\text{gallon}} \times \frac{1 \text{ ton}}{2000 \text{ lb}} \times \frac{1 \text{ process}}{0.48 \text{ efficiency}}$$

= 100 ODT/day (Oven Dry Tons / Day).

The detail breakdown of the cost factors are shown in table 9¹. The cost data has been updated for mid 1981 U.S. dollar value. It is assumed that the plant is being built in a developed/industrial nation.

A comparison of the investments requirements for a 50 million gpy and 200 million gpy methanol facility utilizing natural gas, coal and wood waste as feedstock, is given in figure 12¹. All values are based on 1975 costs and maybe updated to 1981 values using a CE index ratio for 1981/1975 = 1.59.

From table 9, it is noted that the PFI investment which most LDCs have to import from developing countries amounts to 39.25/90.02 or 44 % of the total investment.

One can easily see that methanol production via coal or biomass is a highly capital intensive venture, which may be a problem for applicability to LDCs.

IX. BASE CASE PRODUCT AND OPERATING COST (U.S.A. Based)

The operating costs of a wood waste to methanol conversion plant include fixed costs, labor, raw material and overhead costs. The fixed costs are assumed to be based on a depreciation allowance of 8 percent, a 4 percent maintenance allowance (including labor and material costs) and 2 percent for local taxes and insurance. Profit is calculated assuming a nominal return of 30% on investments equal to 15 percent after federal income tax¹. A typical operating cost estimate for a 50 million gallon/year methanol plant is given in table 10¹.

It should be reiterated that these calculations are all based on U.S. figures. Thus these values should be interpreted accordingly when evaluating the process feasibility for use in LDC'S.

It should be noted that the effect of labor will vary from country to country. For example, a developed country may use only a few workers, due to high labor costs, while a LDC may use many workers, due partly to the higher unemployment rate and the substantially lower labor costs.

Assuming a wood waste cost of \$34/ODT the final product selling cost was estimated to be about \$1.22/gal. Assuming a wood waste cost of \$15/ODTT the final selling price is \$1.03/gal for a 500 million gpy plant.

A comparison of methanol selling prices using natural

TABLE--10
 PRODUCTION COST ESTIMATE AND PRODUCT
 PRICE, WOOD WASTE METHANOL PLANT
 OF 50 MILLION GPY

<u>Fixed Costs</u>	<u>Total</u>	<u>Annual</u> <u>\$ Million</u>	<u>\$/Gal</u>	<u>Percent</u>
Depreciation- 8% investment	7.20			
Maintenance- 4% investment	3.60			
Taxes and insurance 2% investment	1.80			
	<u>\$ 12.60</u>	12.6	0.252	20.6
<u>Raw Materials</u>				
Wood Wastes- 1,500 ODT/Day at \$34/ODT at 340 days/year		17.36	0.347	28.3
<u>Labor</u>				
Operators- 10 stations at \$ 120,000/ year	1.20			
Supervisor- 3 stations at \$ 100,000/ year	0.30			
Administration- at \$100,000/yr	0.10			
Payeoll burden at 30% of labor	0.57			
	<u>\$ 2.17</u>	2.17	0.043	3.5
Overhead- 100% labor		2.17	0.043	3.5
Profit- 30 percent of investment before taxes		27.01	0.540	44.1
TOTAL		<u>61.31</u>	<u>1.225</u>	<u>100.0</u>

Source: Reference -1

gas, coal and wood waste as a feedstock is presented in table 11¹. All values are based on 1975 values.

Another study conducted by Davy McKee, Inc., for a 90 million gal/year methanol plant estimated that to obtain a 15% return on equity (ROE), at a wood waste cost of \$8/metric ton, a selling price of \$0.48/gal would be required. For the same ROE and a wood waste cost of \$4/metric ton, a selling price of \$0.437/gal would be required. A \$12/metric ton requires a 0.522/gallon selling price¹⁴.

A summary of liquid fuels derived from wood via thermochemical processes is given in table 12⁴. A closer perusal of table 10¹ reveals that labor makes up a very small percentage of the field production costs, $0.043/1.225 = 3.5\%$. Thus, although labor costs in LDCs are considerably less than in most developing countries few dollars/day vs. \$12-20/hr, it does not effect the final product cost much. However, the profit derived from such a plant does make up a large percentage of the final product cost, $\$0.540/1.3$, Most LDC ventures would be sponsored by the government, thus there would be no profit factor in the final cost, reducing the selling price to \$0.685/gal.

So if an LDC could meet the large capital investment requirement, it could produce methanol at a price which is competitive with present gasoline fuel costs.

Table 11 --Methanol selling price

	Cents per gallon			
	Production cost	Gross profit	Net profit	Selling price
<u>50 million gpy</u>				
Natural gas at \$1.75/mcf	32.0	14.0	7.0	46.0
Coal at \$38/ton	53.4	44.6	22.3	98.0
Wood waste at \$34/ODT	59.6	38.4	19.2	98.0
<u>200 million gpy</u>				
Natural gas at \$1.75/mcf	25.8	9.2	4.6	35.0
Coal at \$38/ton	41.4	26.6	13.3	78.0
Wood waste at \$34/ODT	57.8	25.2	12.6	83.0

Source: Reference-1

Table 12

Summary of Cost Estimates For Various Liquid Fuels
From Wood Via Thermochemical Processes

Fuel	Source- reference			Commercial facilities could be Available by
	\$/bbl	\$/gal	\$/million Btu	
Methanol	\$28-\$56	\$0.67-\$1.33	\$10.50-\$20.90	Now
Pyrolysis Oil	30-50	0.70-1.20	7-12	Mid to Late 1980's
Ethanol	23-68	0.55-1.62	6.50-19.10	1990's

X. STATUS OF PROCESS DEVELOPMENT

The direct gasification of coal to produce synthesis gas is a proven technology. The subsequent methanol synthesis processes have evolved from the high pressure processes, prevalent in the 1920-1960'S, to the presently more abundant low-pressure processes now dominated by Lurgi and ICI.

Although these processes have been proven utilizing coal and natural gas as feedstock, no methanol synthesis processes, utilizing biomass as a feedstock, have yet been proven at the industrial level. However, with the growing cost of natural gas and fuel costs throughout the world, much interest has been directed towards the use of methanol as a fuel substitute or a supplement, especially in LDCs. Consequently, the demand for methanol is growing.

The distribution around the world of methanol plants utilizing the ICI low-pressure process is given in table 13¹⁷.

Thus the technology for methanol production is advancing. The technology for producing methanol from coal and natural gas feedstocks is well established (see Table 13¹⁷). but is still in the development stages using biomass and wood residues as a feedstock. The Davy McKee Corporation has designed a gasifier to use wood as a feedstock and Chem Systems has designed a process to utilize

Davy McKee experience lies behind most of the large methanol plants built world-wide since 1967.

TABLE- 13

LOCATION	COMPANY	CAPACITY (MTD)	PROCESS	DAVY INVOLVEMENT
USA	Monsanto	910	ICI	
	Georgia Pacific	910	ICI	YES
	Celanese	1800	ICI	YES
	Celanese (1)	1200	LURGI	YES
	Borden	1800	ICI	YES
	Tenneco	930	LURGI	
FAR EAST	Nishi Nihon (Japan)	1000	ICI	
	Taesung (S. Korea)	1000	ICI	YES
WESTERN EUROPE	MCN (Holland)	1000	ICI	YES
	MCN/Dyno (Holland)	1000	ICI	YES
	ICI (England)	1100	ICI	
MIDDLE EAST	NMC (Libya)	1000	ICI	
	Confidential client	2100	ICI	YES
USSR	Techmashimport	2500	ICI	YES
	Techmashimport	2500	ICI	YES

(1) Davy-McKee reformer and detailed engineering.

World methanol capacity using the ICI low pressure process

Licensed Plants	Location	Capacity MTD	ICI Licensee	Status/Start-up	Licensed Plants	Location	Capacity MTD	ICI Licensee	Status/Start-up
Taesung Lumber Company Ulsan	Korea	150	Davy McKee	Onstream	Induquimica, Algeciras	Spain	600	Davy McKee	Onstream
Georgia-Pacific Corporation, Plaquemine, La	USA	910	Davy McKee	Onstream	Taesung Methanol Company Yosu	Korea	1000	Davy McKee	Onstream
Monsanto Company Texas City, Texas	USA	910	Chemico	Onstream	National Methanol Company Marsa El Brega	Libya	1000	Uhde	Onstream
Chang Chun Petrochemical Corporation, Miaoli	Taiwan	150	Davy McKee	Onstream	Societa Italiana Resine	Italy	420	Chemico	1977
Nishi Nihon Sakai	Japan	1000	Kellogg	Onstream	A.E. & C.I. Modderfontein	South Africa	50	Uhde	Onstream
Dor Chemicals	Middle East	150	Humphreys & Glasgow	Onstream	Dyno Industrier A/S	W. Germany	1000	Davy McKee	Shelved
Celanese Corporation Clear Lake, Texas	USA	1650	Davy McKee	Onstream	(a) Celanese Corporation Clear Lake, Texas	USA	1800	Davy McKee	Onstream
Elf Ol, Speyer	W. Germany	800	Humphreys & Glasgow	Onstream	MCN/Dyno Delfzijl	Holland	1000	Davy McKee	Onstream
Almer Arzew	Algeria	300	Humphreys & Glasgow	Onstream	International Minerals & Chemicals/Air Products Sterling, Louisiana	USA	1360	Davy McKee	Shelved
Methanol Chemie Nederland (AKZO/DSM, Delfzijl)	Holland	1000	Davy McKee	Onstream	Techmashimport Gubaha, South Urals	USSR	2500	Davy McKee	1980
P. UK (Ugine Kuhlmann) Villiers St Paul	France	600	Davy McKee	Onstream	Techmashimport, Tomsk, Siberia	USSR	2500	Davy McKee	1980
Metanol SA Camacori, Bahia	Brazil	180	Davy McKee	Onstream	Confidential Borden	Middle East	2100	Davy McKee	1981
Allarco	Canada	1080 (2 x 540)	Chemico	Onstream	Gujarat SFC	India	1800	Davy McKee	1980
Rumanian Ministry	Rumania	600	Uhde	Onstream			60	Linde	1982
China National Technical Import Corporation	China	300	Humphreys & Glasgow	1979	(a) Revamp to High Efficiency Design				
					ICI Plant Billingham	England	300	-	Onstream
					ICI Plant Billingham	England	1100	-	Onstream

Source : Reference -17

wood as a process to utilize wood as feedstock, however it has yet to be proven at the industrial level.

A preliminary study on the production of methanol via fixed bed wood gasification conducted by the Davy McKee¹, ascertained that major areas of uncertainties in the process, are the characteristics and the disposition of the products of wood distillation associated with fixed bed gasification.

These problems must be dealt with before any recommendation can be made for LDCs.

XI.

APPLICABILITY TO LDC'S

By thermochemical conversion and chemical synthesis of biomass numerous liquid fuels can be produced. Liquid fuel is more attractive than biomass derived gaseous fuels because liquid fuel can be produced in one place, stored and transported in conventional containers to another site for use. Methanol, ethanol and pyrolytic oil production have attracted great attention in developing countries.

Methanol yields from wood vary depending upon the type of wood, but a dry ton of wood would produce 80 to 120 gallons of methanol. Methanol production from biomass, like coal, is a two step process. The first step is oxygen gasification of biomass to produce synthesis gas. The second step is to then use the synthesis gas to produce methanol.

The technology, application and operating plant history are numerous for the second step of the methanol synthesis process. Both ICI and Lurgi methanol synthesis processes have been installed throughout the world. But the first step, oxygen gasification of the biomass to produce synthesis gas has yet to be proven in industrial scale production plants. The technology is there but wide spread use or adoption in industrial scale (1000 to 2000TPD) gasification plants could not be found. This may be due to the availability of feedstock, or availability of capital for a new technology. When a fossil fuel is still cheap and its use

involves little capital outlay or equipment design engineering there is little incentive to investigate such alternate energy sources. For whatever reason, not many large scale biomass gasification plants are in operation today.

Furthermore, looking to the technology of both gasification and liquifaction, it may be concluded that its applicability to LDC's should not be considered immediately.

The reasons for such a conclusion are:

- (1) It is a large capital intensive project.
- (2) It requires a large plant capacity to make the plant gate product cost competitive to other fossil fuels.
- (3) It involves the importation of specialized high technology equipment, process technologists, and a high technology equipment maintenance team.
- (4) It requires commitment of a large renewable forestry reserve, planned harvesting, reforestation and a biomass processing facility.
- (5) Even with the limited success of small scale methanol production facilities, there lies considerable technological and economic uncertainty that has to be overcome.

XII. OTHER SOURCES IN THE FIELD

With the rising world fuel costs, the search for an alternate or supplementary fuel source has increased. One, of the most attractive of the alternatives fuels is methanol.

A great deal of research has taken place to synthetically produce methanol. Methanol can be synthesized, utilizing synthetic gas as a feedstock. This synthetic gas can be produced via direct gasification of coal, natural gas, and biomass.

Since most of the process research has been conducted in developed/industrial countries where natural gas or coal are in abundance, these processes have been designed around these two resources. A list of methanol plants licensed by ICI and currently utilizing coal or natural gas is given in table 14¹⁸.

The use of biomass as a feedstock for synthesis gas production has only recently been tested at the industrial level. A list of single-stage fixed bed gasification plants utilizing biomass as a feedstock is given in table 125⁹.

The use of biomass-derived synthesis gas for methanol production has not been tested at the industrial level, although Davy McKee Inc. does have plans to build three plants in India, Canada, and Brazil, in the near future.

C. PLANT LIST

TABLE-14

The following is a list of all low pressure methanol plants that have been licensed by ICI:

<u>Licensed Plants</u>	<u>Location</u>	<u>Capacity STPD</u>	<u>ICI Licenses</u>	<u>Status/ Start-up</u>
Taesung Lumber Co. Ulsan	Korea	165	Davy	On Stream
Georgia-Pacific Corp.; Plaquemine, LA	USA	1000	Davy	On Stream
Monsanto Company Texas City, TX	USA	1000	Chemico	On Stream
Chang Chun Petro- quemical Corp. Miaoli	Taiwan	165 ^(a)	Davy	On Stream
Nishi Nihon Sakai	Japan	1100	Kellogg	On Stream
Gad Chemicals	Israel	165	Humphreys & Glasgow	On Stream
Celanese Corp. Clear Lake, TX	USA	1800	Davy	On Stream
Elf 01, Speyer	W. Germany	880	Humphreys & Glasgow	On Stream
Almer, Arzew	Algeria	330	Humphreys & Glasgow	On Stream
Methanol Chemie Netherland	Holland	1100	Davy	On Stream
PCUK (Ugine Kuhl- mann) Villers St. Paul	France	660	Davy	On Stream
Metanor SA Camacari, Bahia	Brazil	200	Davy	On Stream
Allarco, Medicine Hat	Canada	1200 (2 x 600)	Chemico	On Stream
Rumanian Ministry	Rumania	660	Uhde	On Stream
China National Technical Import Corp.	China	330	Humphreys & Glasgow	On Stream

(a) 165 STD on high carbon feed; 145 STD on low carbon feed.

Source: Reference -18

DAVY BIOMASS, SINGLE STAGE-FIXED BED GASIFICATION PLANTS

TABLE - 15

<u>CLIENT AND PLACE</u>	<u>FUEL</u>	<u>NO. GASIFIERS</u>	<u>YEAR</u>
<u>E. Matarazzo & Co.; Sao Paulo Brazil</u>	Cotton Seed Husks	3	1934
<u>Magadi Soda Works; Kenya</u>	Wood Logs	1	1934
<u>C. Butler Esq.; England</u>	Wood Waste	1	1943
<u>East African Manage. Bd; Kenya</u>	--	1	1943
<u>Soares Irmoas; Portugal</u>	Olive Refuse	2	1945
<u>Fertilizers and Chemicals Travancore Ltd.; India</u>	Wood Logs	6	1945
<u>Kafrel Zayat Co. Ltd.; Alexandria</u>	Cotton Seed Husks	1	1946
<u>St. Kitts Electric Light Dept.; West Indies</u>	Sugar Cane Refuse	1	1947
<u>Ceylon Govt. Poisons Dept.; Colombo</u>	--	1	1947
<u>Fabricas Triumpho; Portugal</u>	Wood Blocks and Chips	1	1948
<u>Mahalakshi Sugar Mills Co., Ltd. India</u>	Bagasse	1	1948
<u>Mozambique Industrial S/A; Portuguese East Africa</u>	Cotton Seed Husks	1	1951
<u>Henry Rogers, Sons & Co., Ltd. South Brazil</u>	--	1	1951
<u>Monapo; Mozambique</u>	Cotton Seed Husks	1	1965-67

Source: Reference -18

XIII.

SUMMARY OF FINDINGS

This report presents the results of the state-of-the-art review of the production of methanol and its derivatives from biomass.

Any carbonaceous material, including lignocellulosic biomass feedstock can be converted to methanol by first undergoing oxygen-gasification, producing synthesis gas which is used as a feedstock for methanol synthesis. The technology of methanol synthesis utilizing natural gas or coal derived syngas has been proven at the industrial level and is practiced widely throughout the world. However, the liquifaction process utilizing biomass derived syngas has yet to be proven.

The results of this study are summarized as:

- * The gasification technology utilized to produce synthesis gas from carbonaceous feedstock, including agricultural, silvicultural and wood residues, is a proven technology.
- * Some feedstock preparation, such as, sizing and drying, may be required before biomass can be gasified to form synthesis gas.
- * All methanol synthesis processes in operation today utilize natural gas, coal, or naphtha, as its feedstock. The feasibility of utilizing biomass as a feedstock has yet to be proven at the industrial level.
- * Recently, several studies have been completed on the production of methanol from wood. These studies confirmed the technical and economic justifications for such an industrial venture.
- * Thermal efficiencies, utilizing coal or natural gas as a feedstock, of around 48% are normal for currently operating low pressure methanol

synthesis processes. Chem Systems synthesis process,utilizing wood chips as a feedstock, projects a thermal efficiency of 57% but has yet to be proven at the industrial level.

- * Environmental tests conducted with methanol fired in a boiler indicate that the emissions of unburned hydrocarbons,sulfer oxides and paticulates are absent. NO_x and CO concentrations were lower than those produced from burning natural gas,and 50 to 70% lower than frcm burning # 2 fuel oil. Also the use in gas turbines showed a significant reduction in the photochemical smog producing elements in NO_x emissions.
- * Methanol is a narcotic and an intoxicant and prolonged exposure requires special safety precautions.
- * Depending upon the cost of wood, methanol can be produced anywhere from \$ 0.67 to \$ 1.33/lb.
- * Methanol's higher compression demands requires some engine redesign before it can be utilized solely as a fuel substitute. However, the cost of redesign should be offset by the savings in fuel costs.
- * Methanol synthesis processing equipment is high technology and will require trained technicians to initially run the plant. This makes the project highly capital intensive and perhaps undesirable for LDC's.
- * A large,inexpensive labor force and government subsidization may make such a venture more cost effective.

XIV.

RECOMMENDATIONS

The need for alternate energy sources is being felt throughout the world. With the rising cost of imported fuel many countries, especially LDCs are watching their hard earned export revenues disappear as they pay the price of imported fuel.

A possible alternate energy source is methanol. Methanol's good heat content (56,560 btu/gal HHV, 49,715 Btu/gal LHV) makes it an attractive alternative to foreign fuel. An area of major interest is methanol's use as a gasoline supplement or substitute. Studies have confirmed that further research is necessary before methanol can be used as a fuel substitute. However, its use as a fuel supplement is promising and has already been tried with great success in Brazil and to a limited extent in the U.S. as "gasohol".

The potential for easing the economic burden resulting from imported oil is greatest in LDCs. The production of methanol via the gasification of coal, natural gas, and naphtha has been proven at the industrial level both technically and economically. The production of synthesis gas which is used as the feedstock for methanol synthesis, via the direct gasification of biomass, has been demonstrated by DM International in installations around the world.

However, the liquifaction technology, utilizing biomass

derived synthesis gas, has not yet been proven at the industrial level, either technically or economically.

It is, therefore, recommended that the following procedures be adopted to assess the viability of biomass derived methanol production in LDC's:

- * Survey the available renewable biomass resources of the country or specific region.
- * Assess the effect on the project of the dependence on outside technical supervision that would be required to operate and train personnel to operate, the high technology methanol synthesis equipment.
- * Assess the country's ability to meet the high capital investment that would be necessary to initiate such a venture.
- * Identify the economic condition of the area and the strength of the labor force available.
- * Since the liquifaction process, using biomass, is still unproven at the industrial level, keep abreast of the recent developments in the field.
- * Set up small methanol operations, solve the problems associated with the process, then move up to larger scale ventures.

Thus, for LDC's where fossil fuels are scarce and expensive and a large biomass resource exists, the production of methanol from biomass derived synthesis gas represents an attractive alternative to fossil fuels. However, since only technologically and economically proven processes can be recommended for use in LDCs it is deemed prudent at this time, that one should wait for the full development of a full scale biomass to methanol conversion plant before recommending its use in LDCs.

REFERENCES

1. Hokanson, A.E. and Rowell R.M.. Methanol from Wood Waste: A Technical and Economic Study. General Technical Report FPL 12, Forest Products Laboratory, U.S. Department of Agriculture, Forest Service. June 1977.
2. Sessler, G.. Synthetic Oil vs. Methanol as a Liquid Fuel Product from Waste Conversion Processes. Submitted to State of California Energy Resources Conservation. Taknekron Inc., Berleley, Ca. March 1977.
3. Engstrom, S. and Lindman, N. A New Synthesis Gas Process for Biomass and Peat. Energy from Biomass and Wastes V Conference, Sponsored by IGT. Jan 26-30, 1981.
4. Congress of the United States Office of Technology Assessment. Energy from Biological Processes, Vol II- Technical and Environmental Analysis. Washington, D.C.
5. Chatterjee, A.K. State-of-the-Art Review on Pyrolysis of Wood and Agricultural Biomass. 53-319-R-0-206. U.S. Department of Agriculture, March 1981.
6. Kohan, S.M. and Barkhodar, P.M. Mission Analysis for Federal Fuels from Biomass Program. EY-76-C-03-0115PA-131. U.S. Department of Energy, January 1979.
7. Imperial Chemicals Industries Ltd. The ICI Low Pressure Methanol Process. P.O. Box 1, Billingham, Cleveland, England.
8. DiNovo, S.T., et al. Preliminary Environmental Assessment of Biomass Conversion to Synthetic Fuels. 68-02-1323. U.S. Environmental Protection Agency, October 1978.
9. DM International. Coal/Biomass Gasification. Houston, Texas.
10. Lurgi Kohle und Mineralotechnik GmbH. Technology of Lurgi's Low Pressure Methanol Process. Bockenheimer Landstiabe 42, D-6000 Frankfurt /M1.
11. Lurgi Kohle und Mineralotechnik GmbH. Methanol by the Lurgi Low Pressure Process. Frankfurt (main).
12. Solar Energy Research Institute. A Survey of Biomass Gasification Vol III- Current Technology and Research. E6-77-C-01-4042. U.S. Department of Energy, April 1980.

13. Kinderman, E.M., et al. Technical and Economic Evaluations of Biomass Utilization Processes. DE-AC03-76ET-20605. U.S. Department of Energy, Sept. 1980.
14. Rooker, J.H. Methanol Via Wood Gasification. Paper presented at IGT's Energy from Biomass and Wastes IV Conference, Jan 21-25, 1980.
15. Chatterjee, A.K. Biomass Conversion Processes For Energy and Fuels. Plenum Publishing Corp. New York, New York 10013.
16. Chatterjee, A.K. Gasification. SRI International, Menlo Park, Ca.
17. Davy Mckee. Information bulletin. Baker street, London WIM IDA, England.
18. DM International. ICI Low Pressure Methanol Process. Houston, Texas.
19. Electric Power Research Institute. Screening Evaluation: Synthetic Liquid Fuels Manufacture. EPRI AF-523. Palo Alto, California. August 1977.
20. Electric Power Research Institute. Liquid Phase Methanol. EPRI AF-693. Palo Alto, California. May 1978.
21. Mawer, D.J. A Modern Biomass Gasifier. DW International, Houston, Texas.
22. Kamp, A. and Goss, J.R. State of the Art for Small Scale (to 50 kW) Gas Production-Engine Systems. 53-319R-0-141. U.S. Department of Agriculture. March 1981.

Akronyms/Symbols/Abbreviations

USDA	United States Department of Agriculture.
AID	Agency for International Development.
LDC	Lesser Developing Country.
HHV	Higher Heating Value.
LHV	Lower Heating Value.
EPA	Environmental Protection Agency.
DOE	Department of Energy.
LBG	Low-Btu Gas.
MBG	Medium-Btu Gas.
ODT	Oven Dry Tons.
EPRI	Electric Power Research Institute.
ICI	Imperial Chemical Industries.
NWC	Naval Weapons Center.
DMI	Davy McKee, Inc.
RCE	return on equity.
TVL	Threshold Limit Value.
scf	standard cubic foot.
psi	pounds per square inch.
psia	pounds per square inch absolute.
TPD	Tons Per Day.
atm	atmosphere.
PFI	Plant Facilities Investment.
ppm	parts per million.
gpy	gallons per year.
bbl	barrel.

NO_x nitrous oxide.

MW MegaWatt.

Btu British thermal units.