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DOE/CE/15459--T5

NATURAL GAS CONVERSION PROCESS

DE93 003629

PROJECT: Build a Laboratory Apparatus and Operate it to provide Data
for a Large-scale Gas Conversion Project

Contract: DE-FG 01-90 CE 15459

SIXTH QUARTERLY REPORT

ABSTRACT:

The experimental apparatus was dismantled and transferred to a laboratory space provided by LBL which is already equipped with a high-ventilation fume hood. This will enable us to make tests at higher gas flow rates in a safe environment. This work will be funded by a CRADA for the LBL expenses and by S-Cal Research Corporation for the direct and indirect costs associated with the transfer of the equipment and of Dr. M. Gondouin as a Guest Scientist at LBL. This project is expected to continue beyond the expiration date of the above contract, with other sources of funding.

Three papers presented at the ACS meeting in San Francisco (Symposium on Natural Gas Upgrading II) April 5-10, 1992 show that the goal of direct catalytic conversion of Methane into heavier Hydrocarbons in a reducing atmosphere is actively pursued in three other different laboratories. There are similarities in their general concept with our own approach, but the temperature range of the experiments reported in these recent papers is much lower and this leads to uneconomic conversion rates. This illustrates the advantages

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of Methane activation by a Hydrogen plasma to reach commercial conversion rates.

A preliminary process flow diagram was established for the Integrated Process, which was outlined in the previous Quarterly Report. The flow diagram also includes all the required auxiliary facilities for product separation and recycle of the unconverted feed as well as for the preparation and compression of the Syngas by-product.

In a recent paper presented on April 1, 1992 at the SPE Regional Meeting, in Bakersfield, CA, information is given about the net pay thickness of the various layers characteristic of the West Sak (AK) Reservoir. These new data have led to the revision of the Fifth Quarter Report estimates regarding the use of a Syngas by-product stream of the Conversion of Prudhoe Bay Gas for the recovery of this heavy oil. Experimental data obtained with the riser/regenerator also show that the composition of this Syngas is essentially CO₂ and H₂, with very little CO. This is in good agreement with the results of G. Samorjai and H. Heinemann (LBL) on the gasification of refinery cokes and coal samples using highly basic catalysts. This has led to a revised material balance for the Integrated Process combining the Prudhoe Bay Gas Conversion Process with the West Sak Heavy Oil Recovery Process, studied under a previous Contract. Conclusions are derived from this material balance regarding the total amounts of liquid Hydrocarbon products obtainable from these presently unexploitable important Domestic Resources.

6. REVIEW OF RECENT PUBLICATIONS ON METHANE CONVERSION IN A REDUCING ATMOSPHERE

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At the recent meeting of the American Chemical Society, in San Francisco, three papers were presented in the Symposium on Natural Gas Upgrading II, which are relevant to the present research because they describe various techniques of Methane activation and conversion to heavier hydrocarbons in a reducing atmosphere, as opposed to most of the previous work, based on oxidative coupling reactions.

The first paper, by a group of French scientists, is entitled: "Homologation of Methane on Metallic Surfaces-Consideration of Reaction Pathways" (Ref.23). The second paper (Ref.24), by a Dutch team, is entitled: "A Low Temperature Reaction Sequence for Methane Conversion". The third paper (Ref.25), by a team from the Argonne National Laboratory, is entitled "The Conversion of Methane to Higher Hydrocarbons Using Molybdenum-Sulfur Clusters Encapsulated in a Molecular Sieve". In all three papers, the activation of Methane into Methyl radicals or into Carbidic specie or other unstable forms resulting from adsorption of Methane on the active sites of the various catalysts used (respectively Ru or Pt on Silica supports, in Papers # 1 and 2, and Molybdenum Sulfide clusters on a Y zeolite support in Paper #3). These unstable specie combine into various multi-carbon chains on the surface of the catalysts and are later desorbed by Hydrogen, as a mixture of hydrocarbons. Paper #1 shows that while the number of unstable adsorbed specie increases with temperature, the Carbon chain growth mechanism and desorption by Hydrogen are favored by much lower temperatures. In all cases, the relatively low adsorption temperature and the acidic catalyst supports used may explain the low conversion rates obtained by these three teams of scientists. The over-all mechanism described here:

Step # 1) activation of CH_4 into CH_3 adsorbed

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on the catalyst surface,

Step # 2) Carbon chain growth and desorption of the heavier Hydrocarbons from the catalyst at a much lower temperature, is similar in principle to that used in our process.

Step #1, in our reactor, is accomplished by exposing the pre-heated CH₄ adsorbed on the colder catalyst to the radicals and atomic Hydrogen generated by the plasma torch.

Step #2 corresponds to the rapid quenching of the radical species on the catalyst particles while these hit the water-cooled conical wall of the cyclone reactor in a zone of the reactor rich in H₂ and CH₄ molecules. The desorbed Hydrocarbon products are then carried away through the cyclone exit into the condensers.

The fact that the product composition in Paper #1 is highly dependent upon the temperature interval between these two steps suggests that the cooling water rate (or temperature of the conical wall of the cyclone reactor) may be an important operational parameter in our process.

This new investigation will be done in Phase 2, after the expiration of the present contract, if sufficient funding is available.

7. PRELIMINARY PROCESS FLOW DIAGRAM OF THE INTEGRATED PROCESS

The Prudhoe Bay Gas raw feed used in the Integrated Process is available at a high pressure ($\geq 1,000$ psi) and relatively low temperature if transported from the Prudhoe Bay NGL plant to any West Sak location through an uninsulated pipeline. The water dew point and Hydrocarbon dew point of that gas are both respectively -40 F.

The preliminary process flow sheet (Fig. 22) makes use of these

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characteristics by using turbo-expanders to bring the raw feed down to the pressure level required by the Cyclone reactor and by its plasma torch. To avoid freeze-up of the expanders, the raw feed gas is further dehydrated in a Mole sieve unit.

The power recovered, in two stages, is used in part for compressing the non-condensed gas product stream from the Gas Conversion unit and in part to re-compress the CO₂-rich residue gas streams from a CO₂-removal Selexol plant. This type of solvent is compatible with a dry gas feed and maintains the water dew point of the purified gas stream at a very low value.

The nearly-adiabatic cooling of the raw feed gas in the expander is used for the cooling cycles of two Temperature Swing Adsorption (TSA) units used respectively to separate in TSA #1 the C₂+ fraction from the H₂, C₁, C₂, CO₂ stream derived from the mixture of raw feed gas and non condensed product-gas from the Prudhoe Bay Gas Conversion Unit, and, after removal of the remaining CO₂ in a Selexol plant, to separate in TSA #2 the C₂+ from the H₂, C₁+ fraction which is sent to a Pressure Swing Adsorption unit (PSA) for separation into a H₂ by-product stream and into the C₁+ recycle stream to the Gas Conversion unit. The combined use of TSA and PSA for the separation of complex streams is presented as the most economic solution in a recent paper by Air Products, Inc. (Ref. 26).

After dehydration in a Glycol unit of the effluent from the riser/regenerator in the Gas Conversion unit, this CO₂, H₂ stream is mixed with the CO₂ stream separated in TSA # 2, compressed and mixed with the H₂ by-product stream for injection as Syngas into the Downhole Reactors of the West Sak wells. The compressors are driven by gas turbines.

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Auxiliary units shown on Fig.22 include a multi-purpose air separation plant,also used as a source of inert gas,and a small Ammonia plant,as in the process flow diagrams of Ref.22.

The main purpose of this preliminary process flow diagram is to serve as a basis for discussion with the Bechtel Group,Inc.to arrive at a rough comparison of capital costs with the Steam Reformer plant described in Ref.22.A complete heat and material balance of the Integrated Process is not yet possible,however,because the Gas Conversion Process is still too far from its optimum operating conditions.It is hoped that this task may be undertaken after Phase 2 of the Natural Gas Conversion Project has provided the necessary data.

8. REVISED MATERIAL BALANCE OF PRUDHOE BAY GAS CONVERSION

Raw Feed Composition:

(Residue from NGL/EOR Plant)

N2	1 (vol %)
CO2	12
C1	80
C2	5
C3+	2

100 moles

Purified Feed:

	Carbon
1	0
0	0
80	80
5	10
2	6

88 moles

96 C

Selectivities Of Conversion Process:

Coke	13 % of C in Purified feed x 96 C/100 mol =	12.48
C2,C3	26	24.96
C4-C10	19	18.24
C10+	42	40.32

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100

96.00

H2 By-product:

Coke	2 moles/C	x	12.48	=	24.96
C2,C3	0.7	x	24.96		17.47
C4-C10	1.2	x	18.24		21.89
C10+	1.4	x	40.32		56.45

120.77 mol/ 100 mol raw feed

Coke conversion in riser/regenerator

$[C + 2 H_2O = CO_2 + 4 H_2 \text{ (} H = +42.4 \text{ Kcal/g.mol)}] \quad \times 2.21$

$[C + O_2 = CO_2 \text{ (} H = -93.7 \text{ Kcal/g.mol)}] \quad \times 1.00$

$3.21 C + O_2 + 4.42 H_2O = 3.21 CO_2 + 8.84 H_2 \text{ (adiabatic)}$

Total By-products per 100 moles of raw PB Gas feed:

$H_2: 120.77 + (8.84 / 3.21) \times 12.48 = 155.14 \text{ mol/100 mol}$

$CO_2: 12 + (3.21 / 3.21) \times 12.48 = 24.48 \text{ mol/100 mol}$

Methanation Reactor Feed: 155.14 H₂, 24.48 CO₂/100 mol raw PB Gas feed

Methanation Reaction: $CO_2 + 4 H_2 = CH_4 + 2 H_2O \text{ (} H = -39.4 \text{ Kcal/g.mol of } CO_2 \text{)}$.

There is a very large excess of Hydrogen in the Methanation reactor feed, indicating that it would be advantageous to recover additional CO₂ from other sources, such as flue gas from the various heaters and boilers required in the auxiliary facilities of the Integrated Plant. If this is economically justified, the potential exists to effectively increase the available volume of stoichiometric Methanation feed, thus also increasing the amount of heat produced in the Downhole Reactors

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9. TOTAL OIL PRODUCTION BY THE INTEGRATED PROCESS

Methanation Reactor Effluent per 100 mol of process raw PB Gas feed: $24.48 \text{ CH}_4 + 48.96 \text{ H}_2\text{O} \text{ (reaction)} + 57.22 \text{ H}_2 \text{ (surplus)}$

Downhole Methanator Heat per 100 g.mol of process raw PB Gas feed:
 $-24.48 \text{ g.mol CO}_2 \times 39.4 \text{ Kcal/g.mol} = -964 \text{ Kcal/100 g.mol}$

Minimum Heat rate from 100 MMscf/D of process raw PB Gas:
 $[100 \text{ MMscf/D} / (38000 \text{ scf/100 lb.mol})] \times 964 \text{ Kcal/100 g.mol} \times$
 $453.6 \text{ g/lb} \times 3.986 \text{ BTU/Kcal} = 4,587 \text{ MMBTU/D or } 191 \text{ MMBTU/h}$

This is approximately 87 % of the heat rate of a reactor of the SPE Paper 22077 co-authored with Bechtel (Ref.22). Recent information published on the West Sak reservoir indicates that smaller reactors (50 % heat rate) would be closer to optimum reactor size, with each well equipped with only 2 pairs of drainholes, instead of 4.

Corresponding West Sak Heavy Oil production (Ref 22) from PB Gas Conversion by-products for a half-size reactor is estimated at 4,000 B/D. Two such reactors would use $100 \text{ MMscf/D} / 0.87 = 115 \text{ MMscf/D}$ of raw PB Gas as process feed and would produce $2 \times 4,000 \text{ B/D} = 8,000 \text{ B/D}$.

Of course, if additional CO_2 is recovered from heater flue gas, the reactor feed composition may be adjusted closer to the stoichiometric. This would increase the reactor heat rate and, conversely, the volume (per mol of feed) of West Sak Oil produced can be increased.

Direct Products of Gas Conversion per 100 lb.mol of raw PB Gas:
 $14 \text{ lb/lb.mol} \times (96 - 12.5) \text{ lb.mol C} / 100 \text{ lb.mol} \times 0.454 \text{ Kg/lb} / 159$
 $\text{Kg/B} = 3.3 \text{ B/100 lb.mol}$

Production rate of Synthetic Crude from 115 MMscf/D of process raw PB Gas:

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$115 \text{ MMscf/D} / 38,000 \text{ scf/100 lb.mol} \times 3.3 \text{ B/100 lb.mol} = 10,000 \text{ B/D}$

Minimum Total Petroleum Products/115 MMscf/D of process raw PB Gas:
 $8,000 + 10,000 = 18,000 \text{ B/D}$

Upside Potential of Total Petroleum Products, assuming full CO₂ recovery from the Integrated Plant fuel, at 70 % thermal efficiency:
 $(100 / 0.7) \text{ mol} - 100 \text{ mol} = 42.8 \text{ mol of fuel raw PB gas} / 100 \text{ mol of process gas, yielding:}$

$(96 + 12) \times 42.8 / 100 = 46.2 \text{ moles of additional CO}_2 \text{ and CO per 100 mol of raw PB Gas used as process gas. This is much more than enough to react with the 57.22 mols of surplus Hydrogen in the reactor effluent which only requires 14.3 to 19.1 mol of CO}_2 \text{ or CO for complete Methanation. A partial (1/4) recovery of the CO}_2 \text{ in the heater flue gas is therefore sufficient to maximize the heat rate (and oil rate) per volume of raw PB Gas consumed.}$

If 80 % of CH₄ produced in the reactor is recycled and mixed with the PB raw Gas feed, the net raw feed gas imported from PB can be reduced to: $100 \times (96 - 0.8 \times 24.48) / 96 = 79.6 \text{ mol per 100 mol of process feed.}$

This would reduce the process gas required from 115 MMscf/D to $115 \times .796 = 92 \text{ MMscf/D}$. The total gas consumed is then $92 \text{ MMscf/D} / 0.7 = 131.4 \text{ MMscf/D}$, assuming that the plant has a 70 % thermal efficiency.

The Net Material Balance is then: $18,000 \text{ B/D} / 131.4 \text{ MMscf/D} = 137 \text{ B / MMscf of raw gas imported from Prudhoe Bay}$

The volume of re-injected gas into the Prudhoe Bay reservoir is expected to reach 7 BCF/D in 1994 when the expanded compression plant is completed. The corresponding additional oil production possible from this Integrated Process, assuming a 70 % thermal efficiency, could reach:

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$(7000 \text{ MMscf/D}) \times 137 \text{ B/MMscf} = 959,000 \text{ B/D}$, of which nearly 45 % may come from the West Sak reservoir when CO₂ is partially recovered from heater flue gas.

With about 25 Tcf of PB gas reserves remaining after deduction of the fuel consumed for oil production at Prudhoe Bay, the total oil production potential of this integrated process is:

$25,000,000 \text{ MMcf} \times 137 \text{ B/MMscf} = 3.4 \text{ Billion B}$ which could be produced in about 10 years at the rate of 0.95 MM B/D.

10. COMPARISON OF WEST SAK OIL RECOVERIES BY THE INTEGRATED PROCESS AND BY THE PROCESS STUDIED WITH BECHTEL

The volume of oil recovered from the West Sak reservoir by the Integrated Process is only about 1.5 Billion B, from a total OOIP of 13 to 25 BB, indicating a 6 to 11.5 % recovery. This may be compared with the recovery from the West Sak by using Syngas made from Steam Reforming in Ref. 21. The small net pay thickness of the lower zones of the reservoir, which dictates the use of half-size reactors and thus doubles the number of well sites, also reduces the estimated ultimate recovery by half, to only 22%. With OOIP of 13 to 25 BB, this corresponds to a cumulative West Sak oil production of 2.9 to 5.5 BB, which may be significantly larger than that obtainable from the Integrated Process

Assuming the same thermal efficiency of 70%, and 80 % recovery of the Methane produced in the Downhole Methanators, the Steam Reformer process, revised for the use of half-size reactors in 4 wells producing only at the average rate of 4,000 B/D, consumes only:

$(441 \text{ MM BTU/h} \times 24 \text{ h/D}) / (1000 \text{ BTU/scf} \times 0.7) + 480 \text{ lb.mol/h} \times 24 \text{ h/D} \times 380 \text{ scf/lb.mol} = 19.5 \text{ MMscf}$ to produce 16,000 B of oil (or an oil yield of 920.5 B/MMscf instead of 137 B/MMscf using the Integrated

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Process.

The cumulative consumption of PB Gas to recover ultimately 2.9 to 5.5 BB from the West Sak by the Steam Reformer Process is then only: $(2,900,000,000 \text{ B} / 16,000 \text{ B/D}) \times 19.5 \text{ MMscf/D} = 3.5 \text{ Tcf of PB Gas.}$

to:

$(5,500,000,000 \text{ B} / 16,000 \text{ B/D} \times 19.5 \text{ MMscf/D} = 5.7 \text{ Tcf of PB Gas.}$

This would leave 21.5 to 19.3 Tcf of PB Gas for the Gas Conversion Process. If the Integrated Process is then used, its by-product Syngas and the corresponding additional heat available may further increase the amount of recoverable West Sak oil by at least 0.8 BB produced together with the Synthetic Crude oil.

This indicates that the optimum use of the PB Gas and of the West Sak recoverable reserves might require the use of both processes in different areas of the field, and probably at different periods.

This would allow to recover from the West Sak Heavy Oil reservoir from 2.9 to 5.5 BB plus about 2.6 BB to 2.3 BB of Synthetic Crude from the Prudhoe Bay Gas Conversion, over the 30 years life of the West Sak field. The Prudhoe Bay Gas Conversion Plant could come on stream around year 20, after depletion of about 2/3 of the West Sak reserves. This leaves ample time to refine the Integrated Process, provided that the Steam Reformer Process, or an other known Syngas fabrication process is first optimized and implemented on the North Slope of Alaska before the time window of opportunity closes.

After 30 years of thermal oil recovery from the thickest layers of the West Sak reservoir, enough viscosity reduction by heat losses may have taken place in the underlying thinner layers to justify their exploitation, using presently shut-in gas resources at Point Thompson, as a source of energy or of injectant in those very thin

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zones, which are presently uneconomic with any known oil recovery process.

Development of the Ugnu reservoir may also use the same approaches. Again, very little information is available in the literature about this reservoir, other than its estimated OOIP of 6 Billion Barrels. Ugnu may be developed concurrently with the West Sak. Even with a conservatively assumed recovery ratio of 30%, it could bring to market an additional 1.8 BB during the same period, using Point Thompson Gas.

Finally, in his testimony before Congress, Admiral J.D. Watkins indicated that the DOE predicted shut-down of TAPS in 2009, in the event that no additional oil production to that of the existing fields be available, from ANWR or from other sources such as those listed above. This would also result in the abandonment of about 1.0 BB of recoverable oil in the currently exploited reservoirs. An additional benefit of bringing on-stream the Heavy Oil production and/or Prudhoe Bay Gas Conversion projects in time to avoid this premature TAPS shut-down would be the additional recovery of 1.0 BB from the existing fields.

11. CONCLUSIONS (Supersedes the Conclusions of Quarterly Report No.5)

Despite the much lower oil recovery ratio (22 %) now estimated for the West Sak, based on the recent reservoir data (Ref.27) published by the University of Alaska (SPE 24038), and the conservative assumptions regarding the Ugnu reservoir, it appears that the proposed research program may still lead to the production of 7.3 to 9.6 Billion Barrels of oil from presently unexploitable domestic petroleum resources in Alaska, plus 1.0 Billion Barrels from the existing fields, which would otherwise be lost. The cumulative production from these various sources

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(8.3 to 10.6 Billion Barrels) is comparable with that of the Prudhoe Bay field, which currently provides more than 15 % of the US Domestic Oil Production.

The present conservative estimate of the magnitude of the targets addressed by this small R. & D. project justifies a concerted effort of commensurate importance to implement the corresponding industrial projects during this relatively short time window. For comparison, the Prudhoe Bay field, over the years since its discovery, has required a Cumulative Capital Investment in excess of \$ 15 Billion.

Its production decline, at a rate of 10 to 12%/year, started in 1989, after 13 years of peak oil production and is expected to demand additional investments in the years to come, in order to maximize oil recovery before the predicted TAPS shut-down date of 2009. Some of these future investments and the large Prudhoe Bay field abandonment costs might be deferred for many years if the Heavy Oil Production and Prudhoe Bay Gas Conversion projects came on stream before that date. The present value of these deferred future costs may exceed \$ 5 Billion.

This brings the Total Capital Cost allowable for the combined West Sak, Ugnu and Prudhoe Bay Gas Conversion projects in the range of \$ 20 Billion to be competitive with the Prudhoe Bay economic results, assuming that oil prices, royalties and taxes remain comparable, in real terms, over the respective production lives of all these projects, including Prudhoe Bay.

Based on the cost data provided in Ref. 22, and even with the developed area in the West Sak, corresponding to the basic 4 Steam Reformer trains described in that paper, now increased from 12 to 24 sq. miles for 65,000 B/D, it appears possible to keep the Total Capital

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Cost, in constant Dollars, within this allowable range.

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FIG. 22 PRELIMINARY PROCESS DIAGRAM

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FOR WEST SAK PLANT

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GAS CONVERSION UNIT **REACTOR FEED PREPARATION** **RECYCLE AND GAS CONVERSION FEED PREPARATION**

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