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Economics of the Oxidative Coupling of Methane as an Add-on Unit for Naphtha Cracking

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Dedicated to Professor Dr. Manfred Baerns on the occasion of his 60th birthday

The feasibility of methane coupling as an add-on unit to a naphtha cracker was studied. The existing cold box was used for separation of ethylene and unconverted methane, but arrangements were made for separation of the coupling by-products. The cracker's methane was used as a feedstock. The concept is technically and economically feasible at spring 1992 prices, provided the catalyst meets the assumed 30% conversion and 80% C₂ selectivity.

1 Scope

The oxidative coupling of methane provides a potential alternative route for the production of ethylene [1]. A major constraint for application however is the, relatively, low yield. High conversion and low selectivity are unattractive in view of the costs of the feedstocks methane and oxygen. Low conversion and high selectivity on the other hand require an expensive cryogenic separation stage, often designated as a cold box, and extensive process equipment in order to recycle unconverted methane.

The present study considers methane coupling as an add-on unit to a naphtha cracker, which concept holds several promises. Fig. 1 shows the principle schematically. Use of the existing cold box avoids the need for investment in expensive cryogenic equipment, although minor adaptations will be necessary for separation of the coupling by-products carbon dioxide and water. Moreover, use of the cracker's methane as a feedstock allows upgrading of the methane, which has a very high purity compared to methane from natural gas, yet is normally used as a fuel of lower heating value. Finally, such an add-on unit improves the flexibility of the cracker's product distribution, which is of advantage in comparison to a mere capacity enlargement by installing another cracking furnace.

The technical and economic feasibility of this concept was studied against the background of a capacity enlargement of 50000 metric tons/year ethylene via methane coupling for an existing naphtha cracker with a capacity of 500000 metric tons/year ethylene.

2 Methane Coupling Reactor

Fluidised bed reactors seem most suitable for methane coupling as the reactions are highly exothermic and this type of reactor approaches isothermal operation [2, 3]. Such a reactor was designed on the basis of a simplified kinetic model [4, 5] for a Li/MgO catalyst, which is still one of the best performing catalysts. A single pass methane conversion of 30% and a selectivity of 80% towards C₂ products were assumed. The kinetic network consists of parallel routes from methane to carbon oxides and C₂ products, and a consecutive step from C₂ products to carbon oxides. Carbon monoxide and dioxide are produced in a ratio of 1:1, ethane and ethylene in a ratio of 2:3.

The well-known two-phase model [6, 7] was applied for the reactor design. The assumptions made were: isothermal operation; plug-flow in the bubble phase; ideal mixing in the dense phase and reaction only in the dense phase. The corresponding non-linear algebraic equations were solved, the bed height being determined by the condition of 99% oxygen conversion above the bed. It was assumed that, at the reactor temperature of 1073 K, the ethane produced was cracked to ethylene in the free-board of the fluidised bed with a conversion of 60% and a selectivity of 82%.

The methane reactor feed was taken from the top of the naphtha cracker's demethaniser and contains almost 99

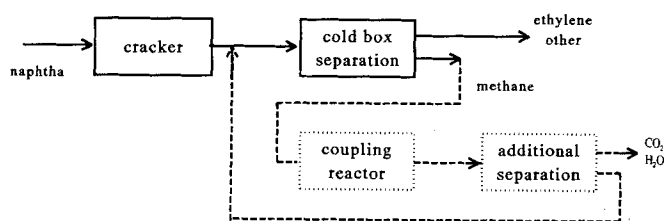


Fig. 1. Schematic representation of methane coupling as an add-on unit to naphtha cracking. Full lines, existing equipment; dotted lines, new equipment.

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wt% methane. The oxygen feed is assumed to come from an external supplier.

The results of the design calculations are shown in Figs 2 and 3 and in Table 1 for model parameters, listed in Table 2, that were obtained from conventional correlations in the literature. Fig. 2 shows a continuing increase of methane conversion and C_2 selectivity in higher beds. The phenomenon is probably due to the combination of the assumed ideal-mixing of the dense phase, leading to lower oxygen concentration in larger bed volumes, and the kinetics, which favour C_2 products at low methane-to-oxygen ratio. The assumption of ideal dense phase mixing will no longer hold at large reactor height over diameter ratios. The required methane conversion of 30% and C_2 selectivity of 80% are already met at a bed height of 7 m, but the oxygen conversion is still below 95%. A bed height of 11.5 m is needed for an oxygen conversion of 99%.

Fig. 3 illustrates that the maximum yield is obtained at a methane-to-oxygen ratio of around 3, which was applied in the final design, summarised in Table 1. Two fluidised bed reactors are needed for the add-on unit's capacity.

3 Process Design

Table 3 compares the compositions of a typical flow into a naphtha cracker's separation section and the flow coming out of the designed methane coupling reactor. The extra carbon monoxide throughput for the cold box resulting from methane coupling is fairly easily removed together with hydrogen as a low value heating gas. The large increase of the methane flow requires adaptation of the heat rating of the demethaniser's reboiler. Ethylene and ethane flow rates increase only marginally. Additional provisions should, however, be made to handle the relatively large amounts of carbon dioxide and water produced by the methane coupling reactions.

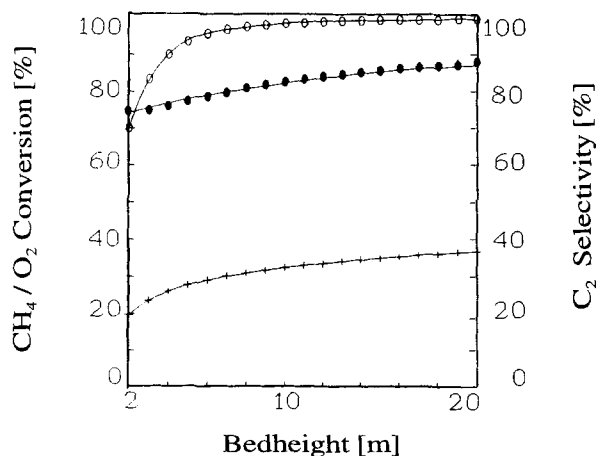


Fig. 2. Conversion and selectivity as function of the reactor height. + Methane conversion, ○ oxygen conversion, ● C_2 selectivity.

Table 1. Dimensions and performance of the fluidised bed reactor.

Ethylene production [Mton/y]	50 000
Reactor height [m]	11.5
Reactor diameter [m]	5.7
Reactor temperature [K]	1073
CH_4 Conversion [%]	33
C_2H_x Selectivity [%]	84
O_2 version [%]	99
Reactor duty [MW/reactor]	18
Number of heat exchanger tubes	55
Length of the tubes [m]	10.5
Diameter of the tubes [m]	0.05

Table 2. Model parameters used in the fluidised bed design.

Minimal fluidisation velocity	0.12 m s^{-1}
Superficial velocity	1.19 m s^{-1}
Interstitial velocity	0.27 m s^{-1}
Fraction emulsion gas in bed	0.45
Max. bubble diameter	0.2 m
Bubble rise velocity	2.2 m s^{-1}
Exchange coefficient	2.0 s^{-1}
Overall heat transfer coefficient	$450 \text{ W m}^{-2} \text{ K}^{-1}$
Cooling temperature	673 K

Table 3. Composition of the naphtha cracking and methane coupling effluent.

Component	Naphtha cracking [kmol/h]	Methane coupling [kmol/h]
Hydrogen	1065	44
Carbon monoxide	7	55
Methane	1773	1420
Acetylene	47	—
Ethylene	2087	230
Ethane	454	46
Propadiene	49	—
Propylene	635	—
Propane	9	—
Butadiene	190	—
Butane	148	—
Carbon dioxide	1	55
Water	356	682

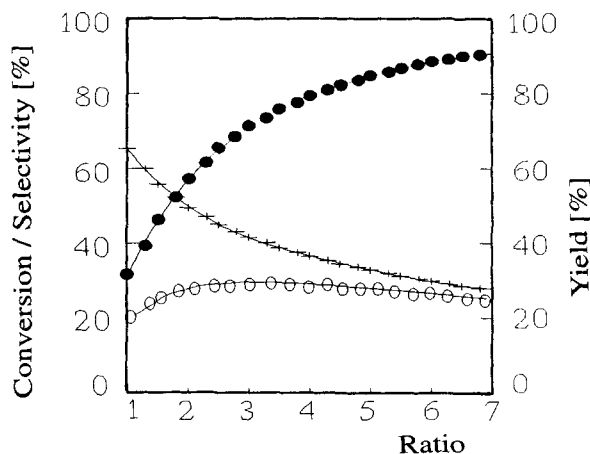


Fig. 3. Reactor performance as function of the molar feed ratio CH_4/O_2 at a bed height of 11.5 m. + Methane conversion, ● C_2 selectivity, ○ C_2 yield.

The new separation section for the methane coupling reactor was designed with the aid of the flowsheet simulation package Chemcad [8] and is shown in Fig. 4. The product stream leaves the reactor at 1023 K and 1 bar and enters the separation section as stream 1. The stream is cooled down to 298 K and condensed water is separated in a knock-out drum. The compression to 10 bar before entering the MEA tower via stream 12 occurs in three steps with interstage cooling to 298 K and water removal. In the MEA tower carbon dioxide is removed from the product stream with a 17 wt% aqueous monoethanolamine (MEA) solution. The liquid stream 21 leaving the MEA tower has a temperature of 379 K on entering the MEA regeneration section, where carbon dioxide is removed via steam-stripping at 1.5 bar. The stripper's bottom stream 22 is cooled and recycled to the MEA tower as stream 27. The top stream 28 from the stripper is cooled and liquid and gas are separated in a knock-out drum. The liquid stream 30, containing mainly water, is recycled to the MEA regeneration tower. Downstream of the MEA tower the top product stream 13 is compressed to 36 bar in two steps with interstage cooling and water removal. The resulting stream 19 is dried with molecular sieves by two dryers in parallel.

The product stream 20 enters the separation section (not shown) of the naphtha cracker right into the cold box, i.e.

downstream of the primary fractionator, quench column and their corresponding MEA tower and dryer.

4 Methods of Economic Evaluation

The fixed capital investment for the designed plant was estimated as a so-called budget estimate via two methods, which both are claimed to have an accuracy of $\pm 25\%$.

1. The specific factor method [9] as developed by the Dutch Association of Cost Engineers (DACE) for estimating battery limits investments distinguishes five groups of process equipment, each with factors depending on the free-on-board (FOB) equipment cost in the base year 1981. Multiplication of the bare equipment cost by this specific factor gives the fixed capital investment without allowance for contingency. The method involves estimation of the bare equipment costs in 1981 and updating by means of cost indices. A 5% contingency was added to obtain the total capital investment.

2. The Miller method [10] is a factored estimation, based on the sum of the free-on-board costs of the main process items (MPI). Other cost items are expressed as percentages of MPI, which are recommended as low, average or high esti-

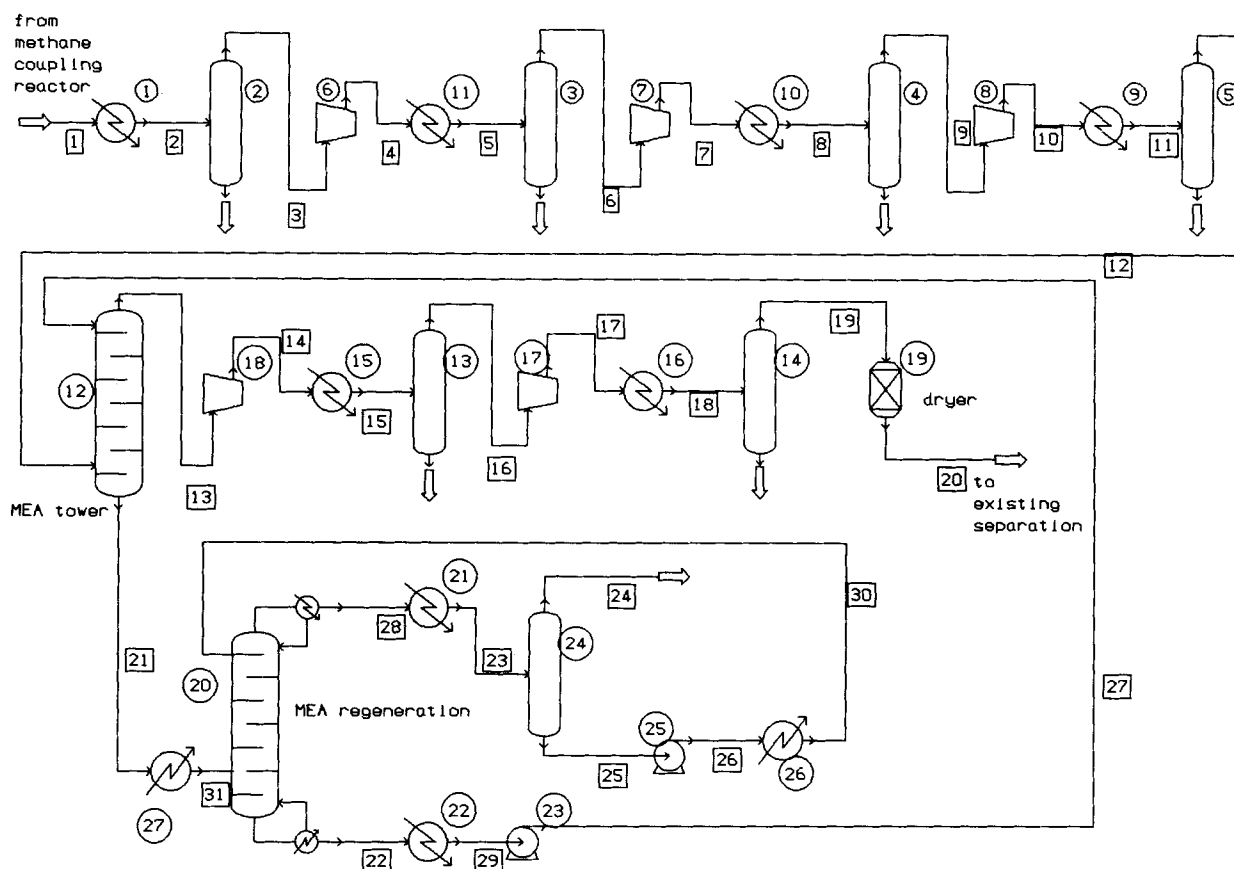


Fig. 4. Additional separation section for treatment of the coupling reactor's effluent, when incorporating oxidative coupling of methane as an add-on unit in an existing naphtha cracking plant. Circles, equipment numbers; squares, stream numbers.

mation factors. In this study all factors were set at the advised average values [10] with some exceptions. The miscellaneous unlisted equipment (MUE) was fixed at the highest value of 20% because the flowsheet is in a rather preliminary stage. Installation of basic equipment was set at the average value for mild steel equipment. The foundation was taken at an average value with addition of 25% for piling. For piping a value of 33% was chosen because most streams contain gases. Insulation was set at a high value owing to the high temperatures involved. Electrical equipment is estimated as comparable to petrochemical plants. Instrumentation was chosen at a high level, because it has developed enormously during the past decades. For buildings and corresponding services average values were chosen with the exception of sprinklers, which were chosen high. The total of factors, leading to the direct costs of battery limits, is 90%.

Factors for other direct costs such as storage and handling, utilities and services were taken low at 12%, because the plant is an additional unit on an existing site.

Indirect costs and contingencies were accounted for by a factor of 25% and 5%, respectively, of the total direct costs. The total capital investment was obtained by adding the working capital, estimated as the revenues of sales during two months. The costs of land were not taken into account.

FOB costs for equipment were determined with the program Chemcost [11] and were partly checked by KTI. The cost estimation of the methane coupling fluidised bed reactor is based on a kettle reboiler made of cast iron. Heat exchanger costs are based on the heat transfer surface area, calculated from the heat duty and the logarithmic driving force, while adopting common values for the heat transfer coefficients. A maximum surface area of 1000 m² was assumed. Therefore the heat exchanger for recovery of the sensible heat from the coupling reactor's product stream was split up into 42 items. For this particular heat exchanger stainless steel was chosen, all the others being made from carbon steel. Refrigeration was incorporated to provide cooling that could not be achieved by process water.

All compressors were considered as motor driven centrifugal compressors. Flash drums were calculated as being positioned vertically, and made of carbon steel. The CO₂ absorber is a tray column, made of carbon steel. The column with a diameter of 1.8 m and height of 12.5 m contains 25 trays. For calculation of the costs of the MEA stripper a tray absorber with reboiler, all made of carbon steel was chosen. The diameter of the column is 1.6 m, the height is 12.8 m and the column contains 26 trays. The dryers contain molecular sieves as packing.

A summary of all major process items and their costs is given in Table 4. Column 4 of this table specifies the FOB costs as used in Miller's method. Column 5 of the table concerns the fixed capital investment for installed equipment according to the DACE method.

Table 4. Summary of all major process items and their costs.

Item no.	Process item	Amount	Item cost, Miller, 10 ³ \$	Fixed capital investment per item, DACE, 10 ³ \$
	Reactor	2	4298	9874
1	Heat exchanger	42	731	2193
11	Heat exchanger	1	55	197
9, 10	Heat exchanger	4	48	176
15, 16				
27	Heat exchanger	1	25	98
21	Heat exchanger	1	31	122
22	Heat exchanger	1	83	274
26	Heat exchanger	1	1	7
	Cooling machine	1	248	793
6, 7, 8, 18	Gas compressor	4	524	1569
17	Gas compressor	1	290	929
2	Flash drum	1	43	229
3, 4, 5, 13, 14	Flash drum	5	21	133
24	Flash drum	1	8	61
12	CO ₂ absorber	1	87	453
20	Distillation column	1	53	300
19	Dryer	2	42	251
25	Pump	1	1	8
23	Pump	1	7	31
Miller	Total MPI cost		42707	
DACE	Total Fixed Capital			123503

Table 5. Percentages used in product cost estimation [12].

Cost-type	Basis	Factor
Operating labour	fixed capital	10
Supervision	operating labour	10
Utilities	raw material cost	10
Maintenance	fixed capital	2
Operating supplies	maintenance	10
Laboratory charges	operating labour	10
Patents & Royalties		0
Overhead	operating labour	60
Local taxes		0
Insurance	fixed capital	0.4
Administrative	operating labour	25
Distribution & Sales	total product cost	5
R&D	total expenses	5

Table 6. Costs and credits in the product cost calculation (spring 1992).

Item	Total amount [kton/yr]	Prize [\$/ton]	Total [10 ⁶ \$/y]
Catalyst	0.136	3450	0.5
Methane	78	163	12.7
Oxygen	108	35.5	3.8
Ethylene	50.0	485	24.2
Carbon dioxide	19.4	250	4.9
Energy	18.4 [Mwatt]	0.05 [\$/kWh]	7.4

A standard method was applied for product cost calculation [12]. Details of the various cost items are presented in Table 5. The amounts and prices of reactants and products are shown in Table 6. The catalyst costs refer to depreciation of

the catalyst after one year. The market prices of most chemicals were taken from Chemical Marketing Reporter. All prices refer to the spring of 1992.

5 Discussion

The total capital investment according to Miller's method amounts to \$144 million or \$130 million according to DACE. The agreement is quite satisfactory in view of the claimed accuracy of the methods. Based on the \$144 million investment, the ethylene cost price is \$1423 per ton of ethylene, or \$1177 per ton of ethylene taking by-product credits into account.

However, when considering the investment costs in more detail, see Table 4, the major cost item concerns the 42 heat exchangers intended to recover the sensible heat from the product stream leaving the methane coupling reactor. It is rather obvious that such an investment of \$92 millions, based on DACE, is not justified to save 1.2×10^8 kJ/h latent heat, which corresponds to 20000 tons of methane per year, or \$3 millions per year.

Without any latent heat recovery the total capital investment amounts to \$45 millions or \$33 millions depending upon the method used, if the minor investment for killing the latent heat is neglected. The lowest net ethylene cost price, would then amount to \$348 per ton of ethylene, which should be compared to the spring 1992 market price of \$485 per ton of ethylene. This represents a return of investment ROI between 15 and 20%.

A comparison of the present study with a naphtha cracker capacity enlargement by installing an additional cracking furnace is not straightforward since tactical considerations like flexibility of the product distribution cannot be weighed. Installation of an extra furnace also requires adaptations in the cold box section, but they differ from the case of a methane coupling add-on unit. Such an enlargement is usually carried-out as a revamp of the complete plant, meaning that the required total capital investment strongly depends on decisions whether or not to replace malfunctioning or depreciated equipment. Moreover spare capacity in parts of a plant is usually taken away in practice by debottlenecking and optimisation of the operating conditions with respect to the design specification. In view of these considerations the total capital investment for such a revamp is estimated to exceed \$45 millions in most cases.

6 Conclusions

The application of methane oxidative coupling as an add-on unit to enlarge the ethylene capacity of a naphtha cracker is a technically and economically feasible concept provided the catalyst meets the assumed single pass conversion of 30% and selectivity of 80% towards C_2 -products. It may use the existing cryogenic separation train of the naphtha cracker for purification of the ethylene produced via coupling, and requires only an additional separation section to remove the coupling by-products carbon dioxide and water. Recovery of the sensible heat from the coupling reactor's outlet stream is not worthwhile for purely economic reasons, despite the large amount of heat involved.

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