

EVALUATION OF METHANOL BASED INDUSTRIES

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تقييم الصناعات القائمة على الميثانول

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تنتج الجماهيرية كميات ضخمة من مادة الميثانول تقدر بحوالى 4% من الطاقة العالمية لهذه المادة ، والميثانول يعتبر المادة الخام الرئيسية في عديد من الصناعات الكيماوية ، والتي اهمها الفورمالدهايد وحامض الاسيتيك وكلوريد الميثيل وغيرها .. كما أنه من المؤكد استعماله كإضافة لبزين السيارات بنسبة تتراوح من 3 - 5 % بطريقة مباشرة أو غير مباشرة في صورة مادة (MTBE) . تهدف هذه الدراسة الى التعرف لطرق التقنية المختلفة لصناعة المواد المعتمدة على الميثانول ، واختيار الطاقة الانتاجية المثلى لكل صناعة باستخدام النماذج الرياضية وإيجاد تكلفة الانتاج في كل حالة مأخوذاً في الاعتبار قدرة الاسواق العالمية على استيعاب هذه المنتجات وتقديرات استيعاب السوق المحلى من الدراسات السابقة في هذا المجال . وقد تم التوصل الى أن افضل سعة لمصنع حامض الاسيتيك هي «40,000» طن سنويا ليحقق المصنع عائدا سنويا يبلغ 10% . ومع ان مصنع الفورمالدهايد يؤدي الى عائد سالب عند هذه السعة الانتاجية مما يستوجب تصميم المصنع بطاقة انتاجية لا تقل عن 45,000 طن سنويا ، ونظرا لأن السوق المحلى يستوعب كمية من هذه المادة في المستقبل القريب فان الدراسة توصي بتنفيذه قبل حامض الاسيتيك ، والذي لا يوجد له استعمال في المستقبل القريب بالجماهيرية . وقد درس مصنع الفورمالدهايد كوسيلة لزيادة الدخل القومى وكانت النتائج مشجعة ..

ABSTRACT

Jamahiriya produces about 4% of the total world capacity of methanol. It is expected that the world consumption of methanol will sharply increase in near future as a result of its direct and indirect use as a blend to motor gasoline leading to an anticipated higher prices. Mathematical models are used in this study to assess different technologies of different methanol - based products in order to optimize the uses of methanol in libya and to assess the variations of production capacities on the production cost. Productions of formaldehyde and acetic acid from methanol are evaluated to optimize several perturbations such as the capacity of each plant, the energy cost and the level of operations on the objective function , . Enhancement ratio, pay-out period and rate of return on investment are calculated using the model to assess their sensitivity to the model's parameters. Acetic acid plant produces a rate of return of 10% at relatively small capacity of 40,000 tons/year. Formaldehyde plant has a negative rate of return at a similar capacity. Formaldehyde plant is feasible with minimum capacity of 45,000 tons/year as partial local utilization is projected. Evaluation of formaldehyde plant as a source of generating foreign currency leads to encouraging results.

INTRODUCTION

Oil and natural gas and their derivatives have traditionally been used as main energy sources worldwide . This situation is expected to continue for many decades to come. The major reasons are the availability and the financial considerations. Different technologies have been developed to optimize the processes searching for better economics. During practising these developments, many by-products are obtained as either side streams or kind of impurities to be separated. As a result many products are produced and used in different objectives such as inhibitors, additives, plasticizers etc.

Methanol is a basic petrochemical product obtained from natural gas . It is the starting point for many production chains and processes covering the three broad categories in petrochemical industry classifications, basic, intermediate and final products.

Methanol is the raw material for many petrochemical products such as formaldehyde (Adhesive industry), acetic acid, methyl chloride, chloroform etc. It is expected to be used directly in energy utilization including driving cars in near future. The increased processing ability and varying the products from a certain source-including methanol raises

automatically the enhancement ratio and the value added component derived from that source. Payout period is also expected to be reduced sharply for the whole chain of industry based on that source leading to the improvement of economics including the rate of return on investment. Marketing strategies based on supply-demand balance is one of the major constraints to optimize the methanol production and its derivatives in any country. Joint venture is one of the forms to ease the marketing problem in case of tightly controlled world market for a certain product.

The world demand of methanol stands at 15 million metric tons per year. Libya produces about 4% of this capacity. World demand of the two major methanol derivatives formaldehyde and acetic acid exceeds 19 and 6 millions metric tons per year, respectively.

TECHNOLOGY AND USES

Methanol

It is the basic feed-stock of the processes assessed in this study. Methanol is produced in Libya from methane. The favoured process to produce methanol is the intermediate pressure process (103 atm) at a temperature of 450-520°F, using copper oxide, aluminium oxide and zinc oxide as catalyst. The main uses of methanol is in the production for formaldehyde, acetic acid solvent and lately as fuel. The world supply-demand of methanol is encouraging. It is expected that the demand of methanol will sharply increase in near future.

The use of 3-5% of methanol as a blend to motor gasoline is investigated in many countries and results are commercially implemented. Shortages of methanol as a result will be expected. In small countries such as Libya, 60,000 tons of extra methanol is needed if the blend is approved. Production of formaldehyde and acetic acid will be affected due to the shortage of the raw materials available for the processes. As a result higher prices will be anticipated in future. Although new technologies based on other raw materials may be developed, it will take long time before the developed processes will be commercialized.

Formaldehyde

The main use of formaldehyde is in the resin industry. The chief use of urea-formaldehyde resins is as an adhesive in fibrous and granulated wood products. Melamine-formaldehyde resins are used as decorative laminates in furniture manufacture.

Formaldehyde is marketed in the form of aqueous solution containing 37% of dissolved formaldehyde gas. Small percentage of methanol is present to avoid polymerization during storage and transportation period. There are two well known processes to produce formaldehyde, metal oxide catalyst process and silver catalyst process. The selection of one of

the two processes depends mainly on end uses rather than economical considerations. The metal oxide process is selected where molybdenum oxide-iron oxide catalyst are used at 5-10 psi and at a temperature of 600-700 °F. Methanol is used as a raw material with a rate of 1.18 ton per ton of pure formaldehyde produced. The catalyst is selected to balance thermally the endothermic dehydrogenation with the exothermic oxidation. Summary of the assessment of formaldehyde plant is presented in table (1).

Table 1. Assessment of formaldehyde plant

Plant Capacity Thousand tons/year	30	45	57	72	90
Methanol needed Thousands tons/year	12.6	18.9	24	30.5	38
Cost of raw materials and catalyst	1.6	2.4	3.05	3.88	4.83
Fixed Capital Investment	15	18.8	21.4	24.3	27.6
Working Capital Investment	1.5	1.9	2.1	2.5	2.7
Enhancement Ratio :					
i) Excluding primary Energy Cost	2.83	2.83	2.83	2.82	2.82
ii) Including Energy Cost	2.62	2.62	2.6	2.6	2.6
Pay-out period	5.7	4.5	3.9	3.4	3
Rate of Return	0.56	-1.47	1.84	5.43	13.17

Acetic Acid

Acetic acid is prepared from methanol through the reaction with carbon monoxide. From material balance 0.58 ton of methanol is reacted with 0.61 ton of carbon monoxide to produce one ton of acetic acid. The energy required for the process is estimated at 0.3 fuel oil equivalent ton per ton of the product. The reaction takes place at 500 psi and a temperature of 390 °F. Rhodium is used as a catalyst. The main uses of acetic acid is in the production of acetic anhydride, vinyl acetate and various acetate esters. Assessment of acetic acid plant at different capacities is listed in table (2).

Table 2. Assessment of acetic acid plant

Plant Capacity Thousand tons/year	39	48	77	91
Methanol needed Thousands tons/year	24	30	48	57
Cost of raw materials	2.9	3.6	5.8	10.9
Fixed Capital Investment	20.7	24	33.4	37
Working Capital Investment	4.3	5.9	8.1	9.4
Enhancement Ratio :				
i) Excluding Primary Energy Cost**	2.6	2.6	2.6	2.6
ii) Including energy Cost	2.3	2.3	2.3	2.3
Rate of Return	10	16	33	41

THE MODEL AND CALCULATIONS

Methanol-based petrochemical industry is highly developed with wide variations in technological processes. It is well intergrated industry with many variables that cause change by orderly perturbations from the usual practice of producing methanol. Different technologies of different methanol-based products are assessed using the developed model in an attempt to optimize the production cost. The model is used to evaluate 9 cases. The concentration is based on three different uses of methanol, acetic acid, formaldehyde and gasoline additives. Capacity of each industry is varied in the model with two major constraints the total productions of methanol and the percentage of methanol used in the gasoline-methanol blend.

The different cases in this work are analysed to show the effect of several perturbations such as the capacity of each industry, the energy cost and surplus on the enhancement ratio and the payout period. The surplus is defined as the production capacity of a certain product minus the demand.

It is difficult to treat the surplus as a factor in the model due to the large fluctuations and unstability of petrochemical products in the world markets. This problem is solved through the treatment of surplus as a heating value product. The objective function in this work is selected to represent the total production cost. The optimization of the objective function is subject to the constraint of the limited capacity.

Enhancement ratio and pay-out period together with the rate of return on investment are calculated using the model to assess their sensitivity. The model

is represented by the following equation (1):

$$y = \sum_{k=1}^N h_k f_k + \sum_{j=1}^M H_j (D_j - R_j) + \sum_{x=1}^n (L_x \times x_x)$$

Where

y is the total production cost of the desired product.

$h_k f_k$ represents the cost of raw materials.

H_j is a chemical price.

$(D_j - R_j)$ represents the surplus production which is evaluated in the model as a heating value instead of chemical value. By products are considered as credits.

L_x represents the investment, labour, additives, catalysts and utilities cost.

R_j is the product demand.

X_x is the level of operations which have to be varied to optimize the total production cost.

D_j represents the production capacity.

The enhancement ratio (ER) is calculated using the following equation:

$$ER = (D_j H_j) / \left(\sum_{k=1}^N h_k f_k + E \right)$$

where E is the primary energy cost which is evaluated relatively to fuel oil equivalent ton per ton produced.

The pay-out period is calculated for each industry (methanol, formaldehyde and acetic acid) using the cost index and literature (2) value for the base case.

The fixed capital investment is calculated for each industry (methanol, formaldehyde and acetic acid) using the cost index and literature (2) value for the base case.

Adjustment of the capacity is performed using the following equation (2):

$$C_1/C_2 = (Q_1/Q_2)^n$$

Where C_1 is the fixed capital of the base case plant

with a capacity equal to Q_1 . C_2 is the fixed capital of the same plant at the same year but at a capacity equal to Q_2 . And q is a constant.

The same procedure is followed to evaluate the battery limit (B.L.) cost. The cost is then evaluated based to the Libyan market, a location factor of 2 is used for this purpose.

The following constraints are considered in the model :

1. The total capacities of methanol production is 600,000 tons/year.

This is treated as a supply limitation where $f_i < S_i$ (Where $S_i = 600,000$ tons/year)

2. The process capacity is limited :

$$x_i < Q_i$$

(Where Q_i is the maximum capacity which can be absorbed for Libyan formaldehyde in world market)

3. Evaluation of local and foreign market of a certain production D creates a demand constraint :

$$R_j < D_j$$

4. Maintenance is considered as a percentage of 3% of battery limit per year, while labour is based on the rate of 2.5 Libyan dinars per man hour, Laboratory service is charged at 25% of operating labour.

5. Electricity is charged at 0.39 kwh/lb, process water at 0.1482 gal/lb and cooling water at 32.55 gal/lb. with a cost of 0037 cent/lb. The electricity is evaluated at 8.1 cent/kwh while the process water is charged at 0.45 cent/lb.

6. The plant overhead is charged at 75% of total labour, insurance is treated as 2% of fixed capital per year. The depreciation is evaluated at 10% / year (linear method).

RESULTS AND CALCULATIONS

Methanol is considered as one of the most basic petro-chemical compounds. Large industries depend on methanol as a raw material. Although there is a glut of methanol worldwide at present, the situation will differ completely when oxygenated alcohols will be used with certain percentages in motor gasoline. This direction seems to be implemented in near future. Shortage of methanol and its derivatives mainly acetic and formaldehyde will be faced and this situation will obviously lead to higher prices for these products. This study is based on the production of formaldehyde and acetic acid in Libya. Total capital investments are calculated for different plant capaci-

ties. Enhancement ratio including and excluding primary energy cost and pay-out period are evaluated. Rate of return is obtained for each capacity of each plant. The results are summarized in tables 1 & 2. It is obvious from these tables that better economics will be achieved from larger capacity. However, supply/demand issue worldwide put a limit on the capacity. Negative rate of return is expected when the capacity is lower than 50,000 tons/year of formaldehyde. The maximum rate of return is achieved with a capacity of 90,000 tons/year of 37% formaldehyde. This plant will consume 38,000 tons/year of methanol. Results listed in table (2) show that acetic acid plant is more attractive if market is available. The production cost of acetic acid will be \$ 338/ton at a capacity of 40,000 tons/year. Rate of return is 10% at this relatively small capacity.

However, development of local market utilizing formaldehyde in near future makes it more favourable than acetic acid, although the later has better economics. Local market is expected to be developed locally to produce urea-formaldehyde, melamine formaldehyde and phenol-formaldehyde resins. Ten thousands to 16,000 tons/year may be consumed locally in near future. Assessment of formaldehyde plant from the point of saving foreign currency is considered in this study. Two levels of formaldehyde local needs are evaluated. The amount of revenue associated with import elimination of formaldehyde is considered as positive foreign currency saving. It is balanced against the payments abroad required to cover the cost of maintenance, expatriate labour, catalyst etc. The saving in foreign currency of the formaldehyde plant is indicated in tables (3-4) for two different capacities 30,000 and 45,000 tons/year.

The local demand of formaldehyde is estimated at 10,000 and 16,500 tons/year in 1990⁽³⁾.

SUMMARY AND CONCLUSIONS

Capital investment, enhancement ratio, pay-out period and rate of return are calculated for major methanol-based industries with different capacities. From the results of all cases studied, it is evident that local markets should be developed for the integration of these products. Although international market is hardly to penetrate in present time, future is bright for the products depending on methanol as a feed-stock. This situation will be developed in near future because of the strong possibility of using methanol as a blend in motor gasoline. Production of formaldehyde and acetic acid in Libya, if any should not exceed 5% of the total production capacity of methanol in Libya due to supply-demand limitations. This constraint represents severe limitations on the freedom to select optimal production cost. Although one of the solution to this constraint comes through joint venture agreement, this is not always the best and open alternative. The economics of the two major

Table 3. Total foreign currency revenues

CASE 1. Formaldehyde plant 30,000 tons capacity
with local demand of 10,000 tons/year

YEAR	FOREIGN CURRENCY EXPENDITURE ON PLANT	FOREIGN CURRENCY EXPENDITURE ON WORKING CAPITAL	FOREIGN CURRENCY EXPENDITURE ON PRODUCTION	IMPORT VALUE	FOREIGN CURRENCY REVENUES FROM EXPORT	FOREIGN NET CURRENCY SAVINGS/REVENUES	FOREIGN CURRENCY GENERATED BY RAW MATERIAL	OVERALL NET
-2	-4.500				-	-4.500		
-1	-5.251				-	-5.251		
0	-5.251	-0.450			-	-5.251		
1		-0.450	-1.164	+1.815	+1.337	+1.538		
2		-0.450	-1.204	+2.0	+1.871	+2.779		
3		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
4		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
5		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
6		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
7		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
8		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
9		-0.450	1.204	+2.0	+3.6	+3.946	-1.512	+2.434
10		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
11		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
12		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
13		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
14		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434
15		-0.450	-1.204	+2.0	+3.6	+3.946	-1.512	+2.434

Table 4. Total foreign currency revenues

CASE I. Formaldehyde plant 45,000 tons capacity
with local demand of 10,000 tons/year

YEAR	FOREIGN CURRENCY EXPENDITURE ON PLANT	FOREIGN CURRENCY EXPENDITURE ON WORKING CAPITAL	FOREIGN CURRENCY EXPENDITURE ON PRODUCTION	IMPORT VALUE	FOREIGN CURRENCY REVENUES FROM EXPORT	FOREIGN NET CURRENCY SAVINGS/REVENUES	FOREIGN CURRENCY GENERATED BY RAW MATERIAL	OVERALL NET
-2	-5.625				-	-5.625		
-1	-6.5625				-	-6.5625		
0	-6.5625				-	-6.5625		
1		-0.563	-1.164	+1.815	+1.337	+1.425		
2		-0.563	-1.183	+2.541	+1.871	+2.666		
3		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
4		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
5		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
6		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
7		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
8		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
9		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
10		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
11		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
12		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
13		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
14		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801
15		-0.563	-1.204	+2.0	+6.30	+6.533	-2.268	+8.801

processes to manufacture formaldehyde is not a decisive factor. The ratio of production cost of formaldehyde using silver catalyst process is 1.02 times the molybdenum catalyst. Using 5% of the capacity of methanol in gasoline production is attractive economically if technical problems are solved. Present local and world supply-demand does not justify building new plants for the manufacture of either formaldehyde or acetic acid. However, formaldehyde plant is feasible with minimum capacity of 45,000 tons/year as partial local utilization is projected. Formaldehyde plant is evaluated as a source of generating foreign currency with positive results. Total foreign currency revenues are calculated at different capacities of formaldehyde plant including 30,000, 45,000 and 57,000 tons/year. The calculations are performed at two different levels of local demand at 10,000 and 16,500 tons/year. The overall net is

maximized at 8,8 million dollars at a capacity of 45,000 tons/year with a local demand of 10,000 tons/year. Sample calculations are presented in tables (3) and (4). This work should continue to evaluate the sensitivity of these projects for fluctuations in world market prices.

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