



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

18217

Distr.
LIMITED

PPD.156 (SPEC.)
18 April 1990

UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

ORIGINAL: ENGLISH/ARABIC

PROJECT PROFILE
ON A DOWNSTREAM PETROCHEMICAL PRODUCT FOR THE ARAB REGION:
CUMENE*

Prepared by

UNIDO Secretariat

*Mention of firm names and commercial products does not imply the endorsement of UNIDO. This document has not been edited.

V.90-83849

TABLE OF CONTENTS

	Page
Introduction	1
World Situation of cumene	2
<u>Table No. 1</u> World production of cumene in 1987	2
<u>Table No. 2</u> Consumption and production of cumene and phenol in the Middle East, Africa, Arab Region and India in 1985	3
<u>Table No. 3</u> Cumene and phenol consumption by world regions in 1985	4
Cumene and phenol consumption and demand in the Arab Region	5
<u>Table No. 4</u> Consumption forecast for phenol and some phenol-based products	6
Future demand for cumene and proposed plant capacity	6
Plant location	6
Production specifications	7
<u>Table No. 5</u> Cumene specifications	7
Raw material specifications	8
<u>Table No. 6</u> Cumene Feedstock Specifications	8
Cumene manufacture	8
UOP Process	9
<u>Figure I</u> UOP Cumene Unit - Process flow scheme	9
Unit Performance	10
<u>Table No. 7</u> Cumene Unit - Material Balance	11
<u>Table No. 8</u> Typical specifications of propylene and benzene fed to cumene unit	12
Product Yield	12
<u>Figure II</u> Transalkylation Chemistry	13
<u>Table No. 9</u> Cumene Column Bottoms, Typical	13
Utility Improvements	14
Product Quality	14
Liquid phase alkylation process using AlCl ₃	14
<u>Figure III</u> Cumene manufacture using aluminum chloride	15
Alkylation and transalkylation	16
Alkylate washing	17
Distillation	17
Product Quality	18
Materials of Construction	18
By-Products	18
Effluents	19
<u>Table No. 10</u> Comparison of Vapour- and Liquid-Phase Processes	19
Uses	19
Uses and applications of cumene	20
<u>Table No. 11</u> Substituted phenols used for phenolic resins	21
Uses of phenol and acetone	22
Capital Investment Cost	24
<u>Table No. 12</u> Investment cost estimate for 100,000 metric tons cumene unit	25
<u>Table No. 13</u> Investment cost estimate for 50,000 tons cumene/year plant	26
<u>Table No. 14</u> Production cost of cumene based on 100,000 metric tons/year plant	27
Profitability and other economic parameters of cumene production	28
<u>Table 15</u> Prevailing prices of cumene during 1988-1989	29
Plant Site and Manpower	29
Conclusions and Recommendations	31

SUMMARY OF KEY RESULTS

Title of profile: Cumene

Production capacity	100,000 metric tons/year
Investment cost	47,300,000 US\$
Working capital	10,000,000 US\$
Production cost	48,000,000 US\$
Production value	
(production cost + 10% ROI min.)	52,800,000 US\$
Sales value	50,000,000 US\$
Return on investment (without working capital)	4.2%
Return on investment (including working capital)	3.5%
Location	Iraq, Algeria, Egypt
Plant site	10,000 m²
Manpower	53-55

The above information is based on a US Gulf Coast plant of 100,000 tons cumene per year, 1989, by direct communication with process owner (UOP), and adjusted to Arab Region conditions.

Sales prices are based on average prices of 1985-1989. Also, the pessimistic scenario for rate of near future sales prices is represented, which was forecasted by the study on production of aromatic compounds in Arab countries carried out by AIDO-GOIC, 1988.

خلاصة بأهم نتائج الدراسة

اسم المشروع	انتاج مادة الكيوميين
الطاقة الانتاجية	١٠٠ ٠٠٠ طن متري سنويا
الكلفة الاستثمارية	٤٧.٢ مليون دولار أمريكي
رأسمال التشغيل	١٠.٠ مليون دولار أمريكي
كلفة الانتاج السنوية	٤٨ ٠٠٠ ٠٠٠ دولار أمريكي
قيمة الانتاج	٥٢ ٨٠٠ ٠٠٠ دولار أمريكي
قيمة المبيعات	٥٠ ٠٠٠ ٠٠٠ دولار أمريكي

العائد البسيط على رأس المال

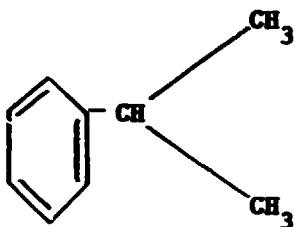
بدون رأسمال التشغيل ٤٢٪
مع رأسمال التشغيل ٣٥٪

المواقع المقترحة	العراق - الجزائر - مصر
المساحة المطلوبة	١٠ ٠٠٠ م ^٢
القوى العاملة	٥٢ - ٥٥ مشغل ومشرف وادارة فنية مع الاحتياط

ان المعلومات اعلاه معتمدة على البيانات التي تم الحصول عليها بشكل مباشر من اصحاب طرق الانتاج UOP لمشروع انتاج الكيوميين مماثل في الطاقة الانتاجية ينشأ في منطقة ساحل الخليج الأمريكي سنة ١٩٨٩ معدلة الى ظروف المنطقة العربية .

اما اعمار بيع المنتج فقد اعتمدت معدلات الاسعار العالمية للسنوات الأربع الماضية ١٩٨٥ - ١٩٨٩ مع اعمار النصف الاول من سنة ١٩٨٩ والتي يبدو بانها تتفق مع السيناريو غير المتفائلة التي تنبأت بها دراسة العطريات في الاقطار العربية في المستقبل القريب .

CUMENE



Introduction

Cumene (isopropylbenzene) is a minor constituent of heavy-aromatic fraction obtained from reforming or pyrolysis operations. For industrial uses, cumene is never recovered from aromatic fractions; rather it is made synthetically by the direct alkylation of benzene with propylene in the presence of a strong acidic catalyst.

The manufacture of cumene was started in the 1930's as a high octane component of aviation gasoline and was extensively used during World War II as a fuel additive to improve the performance of aircraft piston engines. However, it was during the 1950's that cumene established its position in the petrochemical industry. Today, practically all of the world-wide cumene production is consumed in the manufacture of phenols and acetone *).

Phenol is a basic chemical produced in many countries. It has a wide range of high-tonnage uses in the production of phenol-formaldehyde, phenol-furfuryl and other resins. Because of its chemical reactivity, it is used as a raw material in the production of adipic acid, caprolactum and bisphenol - A. Phenol is also used as a component in dyes and insecticides.

Acetone is also an important material used in methyl methacrylates and bisphenol - A production, and is widely used as a solvent and flotation agent.

Although some other derivatives of cumene are of considerable commercial

*) Meyers, Robert. A., Handbook of petroleum refining processes, New York: McGraw-Hill, 1986, p. 1-34

importance, such as hydroperoxide, α -methyl-styrene (AMS), diisopropylbenzene and acetophenone, it is doubtful that any large scale plant would be installed for the manufacture of these cumene-derivative compounds. They occur as by-products during cumene and phenol production and are usually marketed by manufacturers of these chemicals.

World situation of cumene

Total world production of cumene in 1987 amounted to 5,176,000 tons and the future projection indicates that the world production of cumene will be around 5,609,000 tons in 1991 (Table No. 1).

Table No. 1

World production of cumene in 1987 *)

Region or Country	Production (1987)	Projection (1991)
United States **)	1,957,000	2,095,000
Western Europe	1,655,000	1,860,000
Eastern Europe	940,000	1,030,000
Japan	390,000	400,000
South America ***)	102,000	102,000
Rest of the world ***)	122,000	122,000
TOTAL	5,176,000	5,609,000

*) United Nations/Economic and Social Council. Economic Commission for Europe (ECE). Chemical Industry Committee/ECE Chemical market data sheet, 5-7 Oct. 1988

***) Oil and gas journal, 21 March 1988, p. 42

***) 1985 figures have been taken from GOIC-AIDO study on the production of aromatics from naphta, June 1988, Vol. 1, p. 191

The United States produces about 38% of the world cumene, Western Europe 32%, Eastern Europe 18%, Japan 7.6% and the rest of the world only 4.4%.

Data available on cumene and phenol production in India, Africa and the Middle East including Arab countries indicate that no production of cumene existed in these regions up to 1985, but small quantities of phenol are produced in India (19-20 thousand tons), in Africa (8,000 tons) and only 1,000 tons are produced in Egypt. Consumption of cumene and phenol in these regions is relatively just as low as the production level (Table No. 2), and the per capita consumption does not exceed a small fraction of a kilogram.

Table No. 2

Consumption and production of cumene and phenol
in the Middle East, Africa, Arab Region and India in 1985 (1,000 tons)

Region/ Country	Cumene			Phenol		
	Consumption	Production	Balance	Consumption	Production	Balance
Middle East (except Arab reg.)	0	0		9	0	-9
India	26	24		27	19	-8
Africa	0	0		5	8	3
Arab Region	0	0		4.1	1	-3.1
S. Korea	26	26		16	18	2

Per capita consumption of cumene and phenol in the developed regions is relatively high, with cumene ranging from 5.3 kg in North America and 4.2 kg in Western Europe to 2.4 kg in Japan. Per capita phenol consumption was 3.9 kg in North America, 3 kg in Western Europe and 2.1 kg in Japan in the mid 1980's **).

*) Figures abstracted from several sources

***) GOIC-AIDO/Production of aromatic compounds from naptha in the Arab countries: Techno-economic feasibility study, June 1988, Vol. 1, pp. 184-196

The world total consumption of cumene was estimated at 3,816,000 metric tons in 1985 excluding the centrally planned market countries. Total phenol consumption was around 2,873,700 metric tons (Table No. 3).

World demand for cumene grew at a moderate rate of 2% during the 1974-1985 period rising from 3,069,000 metric tons in 1974 to 3,816,000 metric tons in 1985. The growth in world demand between 1980 and 1985 recorded a higher rate of 3.36% per year.

Phenol consumption follows almost the same pattern as cumene with an average worldwide growth rate of 1.75% of the period 1974-1985 and 3.6% between 1980 and 1985.

At a regional level there were wide variations in this rate of growth. North America and Western Europe remain the prime consumers of cumene.

Table No. 3

Cumene and phenol consumption by world regions in 1985
1000s of metric tons *)

Region	Cumene			:	Phenol		
	1974	1980	1985		1974	1980	1985
North America	1,384	1,702	1,829	:	1,079	1,100	1,338
South America	84	125	144	:	63	101	109
Western Europe	1,228	1,070	1,486	:	997	926	1,069
Japan	335	301	284	:	195	220	255
Arab World Trade	0	0	0	:	0	1.4	3.7
Others	38	37	78	:	60	60	99
TOTAL	3,069	3,235	3,816	:	2,374	2,408.4	2,873.7

The total consumption of both North America and Western Europe accounts

*) GOIC/AIDO Study, Production of aromatic in the Arab countries, vol. 1, pp. 183, 190

for about 85% of the total world consumption of cumene and in the developed regions (North America, Europe and Japan) consumption accounts for more than 93% of the world total.

In the United States the annual rate of growth between 1980-1985 was estimated at 1.37% and in Western Europe was about 5.79% while in Japan the rate of growth was at a minus value for the period 1974-1980 at an average of -1.49% and for 1980-1985 at an average of -1.16% indicating a continuous decrease in consumption.

Cumene and phenol consumption and demand in the Arab region

Cumene consumption, as was mentioned before, is determined by the demand for phenol. Over 90% of world cumene is used for the production of phenol; and about half of the phenol produced is used in the manufacture of phenolic resins mainly phenol-formaldehyde. (See uses and applications of cumene and phenol in the following paragraphs.)

Currently, there is neither cumene nor phenol production in any Arab country except for the 1,000 tons produced in Egypt as by-product from coal.

Nevertheless, the Arab region could be potential for phenol consumption in the future if the relevant industries which require phenol in their production either as main material for the production of phenolic resins, bis-phenol A and caprolactam or as chemical and or other minor uses would be developed.

Total consumption of phenol in the Arab region does not exceed 4-5 thousand tons per year currently, and the consumption of phenoplast resins was estimated at 12,798 tons in 1985.

Phenol is also used for the production of caprolactam, which is used to prepare nylon 6. About 50% of caprolactam in the United States is manufactured from phenol where phenol is hydrogenated to cyclohexanone; and upon several reactions caprolactam could be obtained. Adipic acid, which is one of the essential components used for the production of polyamide fibers (nylon 66) could also be prepared from phenol.

The total consumption of the phenol-based compounds was estimated at

28,000 tons in 1985 besides the unknown imported quantities in the form of adhesives or incorporated in plywood, chipped wood and other wooden products. Table No. 4 indicates the forecast for phenol consumption and some phenol-based products in the Arab region.

Table No. 4

Consumption forecast for phenol and some phenol-based products (tons)

<u>Products</u>	<u>1985</u>	<u>1990</u>	<u>1995</u>	<u>2000</u>	<u>2005</u>	<u>2010</u>
Phenol	1,000	1,974	2,363	2,710	3,022	3,306
Epoxide	15,028	15,689	18,154	22,007	24,592	26,925
Phenoplasts	12,798	10,193	11,100	12,058	12,894	13,664

Future demand for cumene and proposed plant capacity

Based on the future demand for phenol, phenoplasts and other phenolic resins and on the indicative plant capacity proposed by the latest studies on the production of aromatic compounds and their derivatives in the Arab Region until 2010, it could be concluded that a plant of 40-50 thousand tons of phenol will cover the requirement for both phenol and phenol-based products. To produce this amount of phenol 56-70 thousand tons of cumene are required.

In spite that 100,000 tons *) of cumene is considered today as a good economic capacity, a 50,000 tons capacity per year could also be adopted.

Therefore, the economic aspects of cumene production in this study will be based on a 100,000 tons per year plant and an alternative of 50,000 tons per year.

Plant location

The main criteria for cumene plant location are the availability of raw materials, the magnitude of local consumption and access for export.

*) Direct communication with UOP, Sept. 1989

According to the current situation of the Arab petrochemical industry, Algeria produces 90,000 tons of benzene per year and Saudi's, Iraq's and Egypt's produced benzene is mostly captive (used within their plants for production of styrene, alkyl benzene and other aromatic-based products).

Propylene is produced only in Libya at present (capacity: 170,000 tons per year). Future plans for Arab petrochemical production indicate that: Iraq will produce 254,000 tons of propylene, Saudi Arabia 265,000 tons and Kuwait 80,000 tons propylene from their refinery.

Based on the present situation and future plans for Arab petrochemical production, Algeria, Iraq and Egypt could be suitable candidates for the accomodation of cumene production. Algeria and Egypt will be supplied by propylene from Libya; and Iraq will have either its own benzene or benzene imported from Kuwait in the future.

Product specifications

The frequently used specifications for cumene are listed in Table No. 5.

Table No. 5
Cumene specifications *)

<u>Property</u>	<u>Test</u>	<u>Value</u>
specific gravity 15.5/15.5	ASTM D 891	0.864 min/0.867 max.
acid wash colour	ASTM D 848	2 max.
bromine index	ASTM D 1492	100 max.
colour	ASTM D 1209	15 max.
sulfur compounds, ppm.		2 max.
product assay cumene, wt%	gas chromatograph	99.9 min.
butylbenzenes, ppm.	gas chromatograph	500 max.
n-propylbenzene, ppm.	gas chromatograph	500 max.
ethylbenzene, ppm	gas chromatograph	500 max.
boiling point, °C		152.39
freezing point, °C		- 96.03

*) Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 7, p. 289

Raw material specifications

The specifications for benzene and propylene (the raw materials required for cumene manufacture) are listed in Table No. 6.

Table No. 6
Cumene Feedstock Specifications *)

<i>Benzene</i>		<i>Propylene</i>	
<i>Quality</i>		<i>Quality</i>	
SG (15.6/15.6°C)			
Range	0.882-0.886		Refinery
Benzene Purity	99.70 wt-% min.		Grade
Distillation Range	1°C max. incl.	Propylene, wt-%	75
(760 mm Hg)	80.1°C	Total C ₂ , wt-%	0.1 max.
Solidification Point	5.35-5.40°C	Ethylene, wt-ppm	100 max.
(anhydrous)		Acetylenes +	30 max.
		Dienes, wt-ppm	
		Butylenes, wt-ppm	1000 max.
Acid Wash Color	1 max.	C ₄ +, wt-%	0.5 max.
Total Sulfur	1 ppm max.	Propane	Balance
Thiopene	1 ppm max.	Basic Nitrogen	0.3 max.
Non-aromatics	about 1500 ppm	Sulfur, wt-ppm	2 max.
Heavy aromatics	500 ppm max.	Water	No free water
Water	No free water		

Cumene manufacture

Cumene as a pure chemical is manufactured exclusively from propylene and benzene utilizing an acidic catalyst (alkylation: Friedel - Crafts reactions).

A wide range of catalysts can be used for alkylation; but in practice, all of the commercial units have been designed to react propylene with benzene

*) Cumene/Phenol - A new look, G.J. Thompson, by H.C. Ward, R.C. Schultz, P.R. Pujado and R.K. Sahlin, U.O.P., Inc. Des Plaines, Illinois, USA

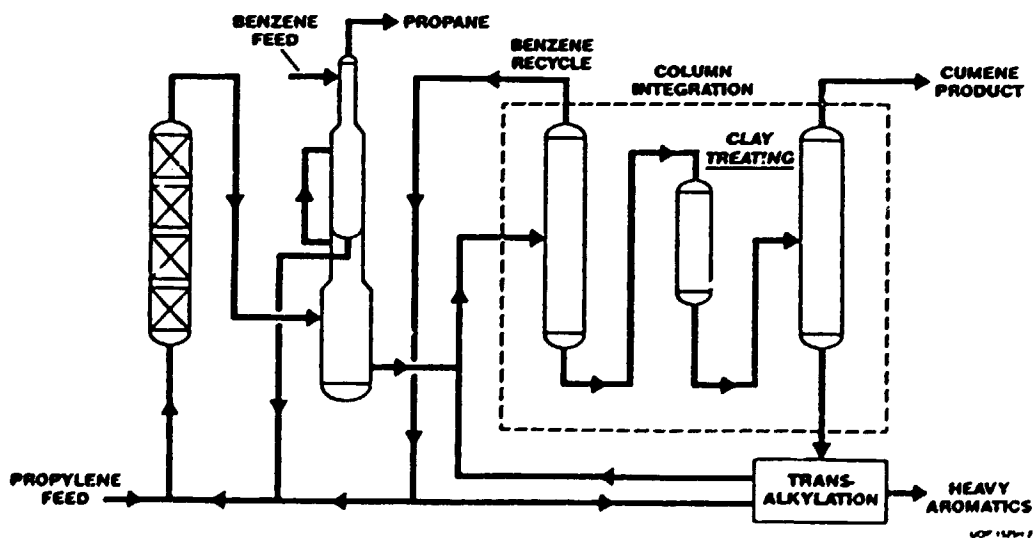
in the presence of sulphuric acid, supported phosphoric acid, hydrofluoric acid, or aluminum chloride. Many different processes and catalyst systems are available, but by far the most important processes now are UOP's phosphoric acid on-kieselguhr fixed-bed vapour-phase process and the liquid-phase aluminum chloride process (Mitsui petrochemicals). UOP's vapour process and Mitsui Petrochemicals' liquid phase process will be reviewed in some detail as typical processes for cumene manufacture.

UOP Process

UOP has licensed and designed more than 40 units for the production of cumene. Of the operating units in the market economies, over 90% have been designed by UOP. This represents a total design capacity of over 3,000,000 metric tons per annum including individual design capacities ranging from 5,000 to 300,000 MTA.

The process flow scheme is illustrated in Figure I.

Figure I
UOP Cumene Unit
Process flow scheme



Fresh propylene feed is combined with recycle benzene before being charged to the upflow reactor. The UOP SPA catalyst provides essentially complete conversion of propylene on a one-pass basis. Adequate benzene recycle is maintained so as to minimize the formation of dialkylated and polymerized product.

The reactor effluent is sent to a preflash section, which serves two primary functions. First, it separates light gases, e.g., propane and lighter, from unconverted benzene, cumene and heavy aromatics. Second, it supplies a portion of the benzene recycle. This second function contributes to utility savings by reducing the quantity of benzene that must be lifted in the benzene column.

Liquid from the preflash section, containing cumene and unreacted benzene, is charged to the recycle column. The remaining benzene is taken overhead and recycled to the reactor. A small amount of recycle benzene is purged from the unit, as required, to prevent build-up of non-aromatics, which have been introduced with the fresh benzene feed and those that result from side reactions. This is sent back to the benzene recovery unit in the plant or blended into gasoline.

The bottoms from the benzene column are passed through clay treating to reduce the olefinicity of the final cumene product, and are then sent to the cumene column where the cumene product is recovered overhead.

The cumene column is designed to reject butylbenzenes and poly-alkylated benzenes from the bottom of the column. A substantial portion of the poly-alkylated benzenes is diisopropylbenzene (DIPB). This DIPB is reacted with benzene and converted to cumene in the transalkylation section of the process. The cumene and unconverted benzene from transalkylation are recovered by recycling back to the recycle and cumene columns. The by-product heavy aromatic stream has a high octane value (109) and can be used as a gasoline octane booster.

Unit Performance

A material balance for a typical 100,000 MTA cumene unit is shown in Table No. 7.

Table No. 7
Cumene Unit
Material Balance

	<i>Feed</i>	<i>Product</i>
Propylene	36,498	
Propane*	12,166	12,166
Benzene**	65,983	
Cumene		100,000
Heavy Aromatics		2,481
Total	114,647	114,647
Total (Propane Free)		102,481

* Assumed present in the propylene stream from an FCC unit.
 ** Excludes benzene in drag benzene

Based on the propylene in the feed and benzene chemical consumption, the yield of cumene is 97.6 wt%. Typical specifications for the propylene and benzene charge stocks are presented in Table No. 6. Refinery grade propylene from a fluid catalytic cracking unit is the most common source for this feed. Benzene is generally supplied from an extraction unit such as the Sulfolane or Udex processes. A somewhat lower quality benzene (lower freeze point or higher non-aromatics content) also can be easily handled by an increase in the benzene drag stream to maintain recycle benzene purity and safeguard product quality.

Table No. 8
Typical Specifications
of propylene and benzene fed to cumene unit

<i>Benzene</i>		<i>Propylene</i>	
<i>Quality</i>		<i>Quality</i>	
SG (15.6/15.6°C)			
Range	0.882-0.886		Refinery
Benzene Purity	99.70 wt-% min.		Grade
Distillation Range (760 mm Hg)	1°C max. incl. 80.1°C	Propylene, wt-% Total C ₂ , wt-%	75 0.1 max.
Solidification Point (anhydrous)	5.35-5.40°C	Ethylene, wt-ppm Acetylenes + Dienes, wt-ppm Butylenes, wt-ppm	100 max. 30 max. 1000 max.
Acid Wash Color	1 max.	C ₄ +, wt-%	0.5 max.
Total Sulfur	1 ppm max.	Propane	Balance
Thiophene	1 ppm max.	Basic Nitrogen	0.3 max.
Non-aromatics	about 1500 ppm	Sulfur, wt-ppm	2 max.
Heavy aromatics	500 ppm max.	Water	No free water
Water	No free water		

Product Yield

The newest of UOP's developments is the transalkylation of cumene column bottoms. Without transalkylation, the cumene yields based on total liquid product are 94.5 wt%. With the addition of transalkylation, the cumene yields can be increased to 97.5-98.0 wt%.

The definition of transalkylation is the reaction of one mole of diisopropylbenzene (DIPB) with one mole of benzene to form two moles of cumene (Figure III). A typical cumene column bottoms composition without transalkylation is shown in Table No. 7. Since cumene column bottoms makes up approximately 5 wt% of the total liquid product, 2.5 to 4.0 wt% DIPB is generally discarded with this heavy aromatic stream.

Figure II
Transalkylation Chemistry

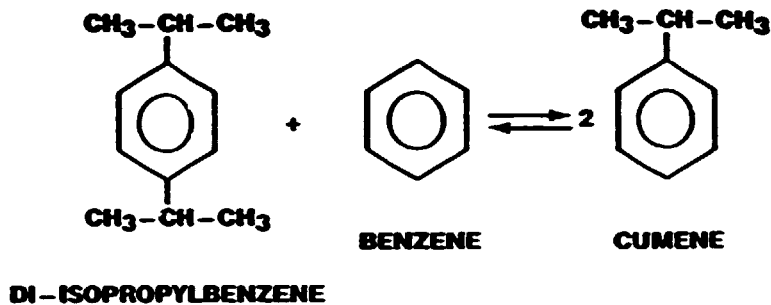


Table No. 9
Cumene Column Bottoms
Typical

	<i>Wt-%</i>
Isopropylbenzene	1-5
Butylbenzene	1-8
Diisopropylbenzene	50-80
Hexyl Benzene -	10-35
Heavies	8-20

The UOP transalkylation technology uses a fixed-bed catalyst system to convert this DIPB, with over 90% selectivity, to cumene. The transalkylation cumene product, consisting primarily of cumene, benzene and some unconverted DIPB, is recycled back to the conventional fractionation train. Recycling recovers the benzene and cumene, and provides a second pass over the catalyst for the unconverted DIPB. As a result, the small yield losses of DIPB are primarily due to fractionation inefficiencies.

Utility Improvements

Over the years, UOP has continued to make design changes that improve utilities. The original design in the late 1950's had a gross heat input of approximately 1,400 cal/g of cumene. The majority of the designs in operation today have improved this value to about 800-950 cal/g, assuming no credit for low pressure steam generation in fractionation. If credit is taken for LP steam, this value can be reduced further to 90 cal/g.

Recently, UOP has made further improvements in the design through modification of the preflash system and heat integration of the columns. The result is a further reduction in utilities to 450 cal/g, without taking a low pressure steam credit. The first commercial application of this technology successfully came on stream in the fall of 1987.

Product Quality

As shown in Figure I, UOP has developed clay treating technology that can reduce a 50 bromine index product to below 10. The same technology can be used to realize a capacity increase and still maintain the 50-100 bromine index specification.

The reduction in olefinic content of the cumene product is accomplished by alkylating the contaminating olefin with cumene to form a heavy aromatic. Clay treating is done on the cumene column feed, so the resulting heavy aromatic can be easily separated from cumene in the cumene column. Since the olefin content is small (ppm range), the cumene yield loss is negligible.

Liquid phase alkylation process using $AlCl_3$

Aluminum chloride is a preferred alkylating agent for laboratory-scale production of many alkyl benzenes, but it was not used for cumene manufacture in the early days of phenol development. It was not until the late 1950's

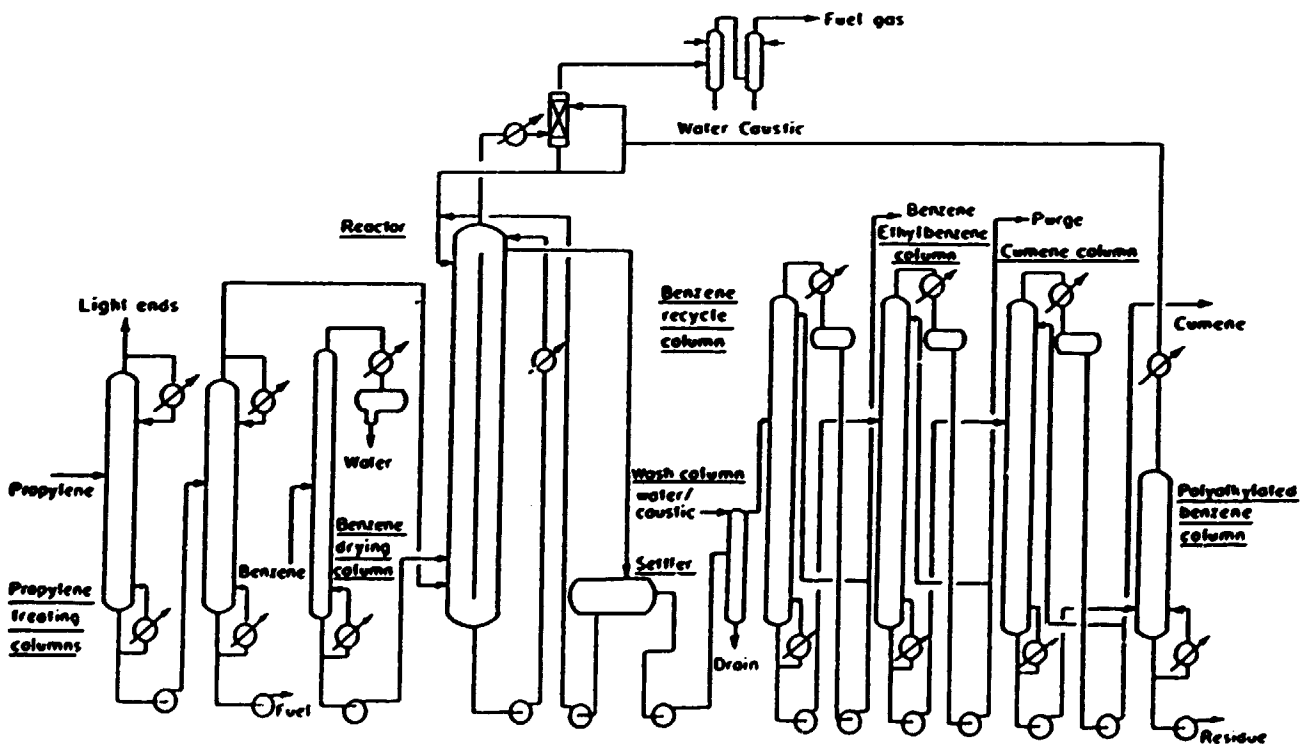
*) McKetta, John J. and William A. Cunningham, eds. Encyclopedia of chemical processing and design, New York, Dekker, 1982, Vol 14, p. 43

that British Hydrocarbon Chemicals (later BP) built the first plant in the United Kingdom, to be followed by Mitsui Petrochemical Industries.

Basically, the design is similar to that of other processes having a feed pretreatment section if required, a reactor system and a distillation section. The reaction conditions, including arrangements for feeding catalyst and recycle of polyalkylbenzenes for dealkylation, are, however, quite different (see Figure II).

If feed pretreatment is required for this process (depending on the quality of feedstock), liquid propylene is dried in a regenerative absorptive drier and fed to a de-ethanizer where C_2 compounds are distilled. The bottoms pass to a propylene column where C_4 's, and heavier, are removed in the base stream.

Figure III
Cumene manufacture
using aluminum chloride



Liquid propylene in the overheads is vaporized and fed to the reactors.

Fresh benzene usually contains too much water for immediate addition to the reactors. It is therefore mixed with recycled benzene and fed to a column containing 20-30 plates for dehydration. After condensation, benzene and water separate in a decanter, which also serves as a reflux drum for the column. Benzene from the base contains typically less than 10 ppm water.

Alkylation and transalkylation

The reaction section usually consists of two or more brick-lined vessels partitioned into "reaction" and "settling" zones, with downstream separators and wash drums. All the reactant and recycle streams are introduced into the reaction zone. Since agitation is required, it is necessary to admit propylene vapour at the base where catalyst complex, which is insoluble in hydrocarbon, tends to settle. The complex is thereby lifted and mixed intimately with the reactants. Aluminum chloride is added to the top of the reactor and the promoter, usually HCl or isopropylchloride, enters with the reactants.

The promoter is essential for stabilizing the catalyst complex, for only a stable complex will catalyze the reaction. This is an important point to note since, during reactor operation, declining activity may be caused by a deficiency of either aluminum chloride or promoter.

It is a particularly advantageous feature of this process that PAB may be recycled to the reactors, as aluminum chloride has the ability to transalkylate PAB in the presence of benzene. However, low cumene output may ensue for, in addition to the points noted above, the reaction is affected by the quantity of PAB returned. Poor activity usually develops as a consequence of attempting to maintain efficient alkylation at a low reactor temperature. The anomalous position is soon reached in which the alkylation step needs to be carried out preferably below 100°C, whereas transalkylation requires a temperature in excess of 130°C. In practice, a compromise temperature of around 115°C is chosen, which often results in neither steady reactor operation nor optimum efficiency. This dilemma may be resolved by transalkylating PAB separately. It is most conveniently carried out in one of the two alkylators if a two-reactor system is installed. This arrangement has

the added advantage of enabling catalyst complex to be prepared in a clean environment, that is, in the alkylator. When aluminum chloride is added to a "mixed" reaction system, it tends to complex with the recycled PAB, giving rise to the formation of tars, and becoming deactivated in the process.

In addition to the gaseous feed to distribute the catalyst complex, there may be provided a pump to recirculate settled complex to the top of the reaction zone as shown in Figure II, and a compressor to recycle propane (obtained from reactor off-gas). This recycled gas ensures efficient mixing of complex and reactants.

Some ethylbenzene units have been constructed where the catalyst complex is prepared in a separate vessel. This procedure does not appear to have any particular merit, however, for alkylation of propylene, and may actually increase catalyst consumption.

Care has to be taken with the reactor off-gas which, in addition to benzene and other light hydrocarbons, contains HCl. The benzene is recovered in an absorber containing recycling PAB, and the HCl is scrubbed out of the off-gas in two towers, one containing water and the other caustic soda solution. The residual gas can be compressed and used as fuel.

Alkylate washing

A catalyst settling drum is provided immediately downstream of the reactors. Complex is recycled from this drum to the reactors, and crude alkylate passes forward to a water wash tower. After most of the complex is removed, the residual acid in the alkylate is neutralized with caustic soda solution.

Distillation

The distillation section has two marked differences from the other processes. First, provision has to be made to remove ethylbenzene from washed alkylate. Depending on the quantity, it may be advantageous to accumulate this material and subject it to a separate batch distillation. The second major difference concerns the material heavier than cumene. This is not

disposed of as fuel, as in the other processes, but is returned to the reactors for transalkylation after removing the heaviest polyalkylbenzenes. The latter operation is usually conducted in a small column under high vacuum.

Product Quality

Aluminum chloride complex readily reacts higher olefins, which may be formed in the alkylators, with aromatics. Reactor product does not therefore contain, for example, propylene oligomers, as in the vapour process, and the cumene finally distilled has a very low bromine number.

Materials of Construction

The presence of HCl in and around the reaction area can be troublesome, and its treatment is a major disadvantage of this process. It is necessary to line the reactors with acid-resistant brick. It may also be necessary to fabricate overhead and downstream pipework in materials resistant to HCl, this requirement extending also to vessels and instrumentation in this area. After the off-gas and alkylate streams have been neutralized, carbon steel can be used.

By-Products

In all processes, by-product removal is relatively simple. Gaseous hydrocarbons can be used as fuel gas after pressurization, and liquid materials are suitable for use in boilers or hot oil systems.

Ethylbenzene concentrate from the AlCl_3 process and purged benzene from the recycle streams of the HF and phosphoric acid processes can provide high octane gasoline components.

DIPB is used as an intermediate for resin manufacture and can be extracted from the PAB stream. PAB itself is a useful solvent for tank cleaning and wood preservative preparations.

Effluents

The phosphoric acid process is required to dispose of only a small amount of water as effluent from the depropanizer. It therefore has an advantage over the liquid catalyst processes whose waste liquor may cause problems, especially when it mixes with effluent from other units. These difficulties can be overcome by controlled use of settling tanks, neutralizing chemicals, and adequate water for dilution, but the cost may not be insignificant. On the other hand, it is necessary to remove catalyst occasionally from the reactors in the phosphoric acid process, and aqueous washings have to be carefully treated to avoid downstream problems.

Table No. 10
Comparison of Vapour- and Liquid-Phase Processes

	Vapor phase (H ₃ PO ₄)	Liquid phase (AlCl ₃)
Reactor pressure (lb/in. ² gauge)	450-500	10
Reactor temperature (°C)	240	100-130
Conversion (%):		
(a) Propylene to cumene	92	96
(b) Benzene to cumene	95	97
Benzene feed	Water removal	Water removal
Propylene feed	LE and HE removal	LE and HE removal
Catalyst	Fixed bed	Continuous addition and removal
Crude product	Filtration required	HCl removal
Distilled product	Removal of propylene oligomers and alkyl thiophene	EB removal
Effluent	—	Settling necessary
High capital cost	Reaction Hot oil system	Reaction area EB column
High operating cost	Catalyst loading and removal Benzene purge Downgrading of PAB Acid washing	Continuous catalyst removal EB column Disposal of catalyst complex

Uses

Mention has already been made of the value of cumene as an antiknock agent in aviation fuels, but now its main outlet is as a starting material in phenol and acetone manufacture. Well over half the world's supply of

phenol-from-cumene is obtained from the BP Chemicals/Hercules process, in which cumene is oxidized directly with air and the resultant hydroperoxide is cleaved with mineral acid. There are variations, e.g., Phenolchemie's use of oxygen rather than air.

Cumene hydroperoxide is used as a curing agent in many peroxide-catalyzed reactions, especially for automobile bodies and heat-resistant resins. It is usually obtained as an 80% concentrate from phenol manufacturers, after the cumene oxidation stage.

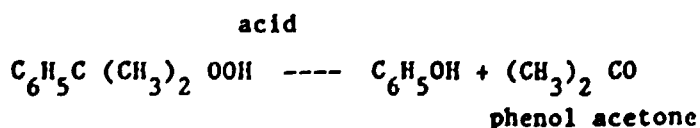
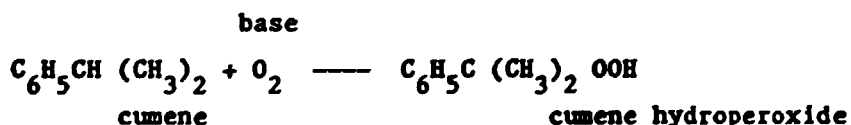
Cumene can be further alkylated with propylene to form p-diisopropylbenzene which can be used as an intermediate in the production of terephthalic acid.

Although α -methylstyrene is often obtained as a by-product during phenol production, there are processes which convert cumene directly. This is a useful starting material for many resin preparations.

Vigorous oxidation of cumene gives acetophenone, which finds application as a specialist solvent in paint and printing ink coatings and in perfumery.

Uses and applications of cumene

Over 90% of manufactured high purity cumene is used in the production of phenol and acetone through cumene oxidation system. Cumene can be oxidized in a basic medium to stable cumene hydroperoxide. Upon acidification, the peroxide is cleanly transferred to phenol and acetone.



After removal of unreacted cumene, acetone and reaction by-products such as α -methylstyrene, the crude phenol product is suitable for plywood resins, bakelite resins, etc. For a pharmaceutical-grade product, further purification is required.

Phenol is the monomer, or raw material used in the largest percentage (40% of production) for making phenolic resins.

Although substituted phenols are used for speciality resins, phenol itself is used in the largest volume (Table No. 11).

Table No. 11

Substituted phenols used for phenolic resins

<u>Substituted phenol</u>	<u>Resin application</u>
cresol (o-,m-,p-)	coatings, epoxy hardeners
p-t-butylphenol	coatings, adhesives
p-octylphenol	carbonless paper, coatings
p-nonylphenol	carbonless paper, coatings
p-phenylphenol	carbonless paper
bisphenol A	low colour molding compounds, coatings
resorcinol	adhesives
cashew nutshell liquid	friction particles

The substituted phenols are typically alkylated phenols made from phenols and the corresponding α -olefin with acid catalysis. The incorporation of alkyl phenols into the resin reduces reactivity, hardness, cross-link density and colour formation, and increases solubility in non-polar solvents, flexibility and compatibility with natural oils.

The second major chemical use for cumene is the production of α -methylstyrene. It is produced by catalytic dehydrogenation of cumene and is used as a copolymer in specialty resin systems.

Other minor uses of cumene include the use of cumene hydroperoxide as a

chain initiator in polymer chemistry.

From the above review, it is quite evident that there are no direct uses or applications of cumene; it is an intermediate aromatic product. Almost more than 90% of cumene produced is used for the production of phenol; and a major portion of phenol produced is used in the production of phenolic resins. Consequently, the consumption of cumene will be tied up with the consumption of phenol (including phenolic resins) and acetone; and the economy of cumene production will, as well, be governed by the prices of benzene, since benzene forms two thirds of the raw materials required and the other third is propylene.

Therefore, it will be useful to review the uses of phenol and acetone, for which cumene is the intermediate, in order to evaluate the viability of cumene in the Arab region.

Uses of phenol and acetone

The three most significant products derived from phenol are phenolic resins, bis-phenol A, and caprolactum. The largest single use for phenol is in phenolic resins, which are produced by the condensation of phenol or a substituted phenol with an aldehyde, e.g. formaldehyde. Phenol-formaldehyde combinations are believed to account for over 95% of phenolic resins. These resins are widely used in major industries, particularly in the construction, automotive and appliance industries. Plywood adhesives also require considerable amounts of phenolic resins.

Bis-phenol A is produced by the reaction of phenol and acetone in the presence of an acid catalyst. The largest markets for bis-phenol A are the production of epoxy resins and in the manufacture of polycarbonate resins.

The thermoset properties characterizing phenolics include high heat resistance, chemical resistance, good dielectric properties, surface hardness, dimensional and thermal stability, relatively low cost, and easy moldability. A wide variety of phenolic resins and molding compounds can be formulated to meet requirements of electrical, electronic, automotive, appliance, and other applications.

Phenolic resins are available in granular, powdered, or liquid forms for bonding and laminating varnishes used in laminates and overlays; foundry sands to make shell molds and cores; waterproof plywood adhesives for the manufacture of particle board, chip board, and fibreboard, insulation foams, bonding adhesive grains in grinding wheels; and the manufacture of brake linings, blocks, and clutch faces.

Phenolic resins of both the resol and novolac types are also combined with other ingredients to make phenolic molding compounds, which are mixtures of resin, filler, reinforcements, colouring agents, lubricants and modifiers.

Household appliance applications continue to make use of phenolics in various custom-matched colours because of their good high-temperature performance in relatively thin cross sections and under load. Also, because of their suitable properties mentioned above, other suitable applications for phenolic compounds include automobile ignition parts, ashtrays, and brake transmission and fuel systems components; steam iron handles and utensil knobs and handles; electrical switch gear, circuit breakers, and wiring devices; piano keys and bottle enclosures.

Acetone is used primarily as a chemical intermediate and solvent. The following list represents the main uses of acetone:

- methacrylate
- solvent (paints, varnish, lacqures and other resin solutions)
- methylisobutyl ketone
- bis-phenol A
- processing solvent
- pharmaceuticals
- spinning solvent (cellulose acetate)
- hexylene glycol
- diacetone alcohol
- methylisobutyl carbinol

and others.

Capital Investment Cost

The capital investment cost for 100,000 metric tons cumene plant per year constructed in a grass roots site in the Arab region is estimated at approximately 47.3 million US\$ plus a minimum amount of 10,000,000 US\$ for working capital Table No. 12.

This estimate was based on a battery limits plant cost in the US Gulf Coast in 1989 using UOP's process adjusted to Arab Region's conditions. Approximate cost of 3 months feedstock has been assumed for the required working capital and 13% of total investment cost has been allowed to cover the interest during construction period.

Investment cost for a 50,000 metric tons per year cumene plant was estimated at approximately 31 million US\$ based on the same principles above plus an amount of 5 million US\$ as working capital (Table No. 13).

A plant built within already existing petrochemical or refinery complex, could save about 50% of the utility and offsites facilities cost by utilizing the existing facilities.

Table No. 12

Investment cost estimate for 100,000 metric tons cumene unit
grass root - 1989 US\$

<u>Item</u>	<u>Cost US\$</u>	<u>Remarks</u>
Erected equipment & materials (battery limits)	10,000,000	US Gulf Coast 1989
Design and engineering	4,000,000	
Utility units (50% of erected B.L.)	7,000,000	
Offsites facilities (50% of erected B.L.)	7,000,000	
Total erected plant	28,000,000	
Adjustment to Arab Region (location factor 1.4)	11,200,000	
Inventory of catalysts and chemicals	937,500	location factor 1.25
Total	40,137,500	
Interest on capital during construction	5,217,875	13% for whole period
Contingencies 5%	<u>2,006,875</u>	
Total investment cost without working capital	47,362,250	
Working capital	<u>10,000,000</u>	
Total with working capital	57,362,250	
	=====	

Table No. 13

**Investment cost estimate for 50,000 tons cumene/year plant
1989 in US Dollars**

Item	Cost US\$	Remarks
Erected plant (battery limits) including design and engineering	9,300,000	US Gulf Coast 1989
Utilities and offsite facilities (100%) of erected	9,300,000	
Total erected cost	18,600,000	
Adjustment to Arab Region's conditions (location factor 1.4)	7,440,000	
Inventory of catalysts and of chemicals	500,000	
Total	26,540,000	
Interest on capital during construction (13%)	3,432,650	
Contingencies 5%	<u>1,302,000</u>	
Total	31,274,650	
Working capital	<u>5,000,000</u>	
Total	36,274,650	
	=====	

Table No. 14
Production cost of cumene based on
100,000 metric tons per year plant

Input elements	Consumption ton/ton	Units price US\$	Cost of production per ton
<u>Raw materials</u>			
Benzene	0.66	322	212.5
Propylene	0.38	380	144.4
Catalysts & Chemicals			10
<u>Utilities</u>			
Electric Power	25 kwh	0.035	0.875
Steam 42 kg/cm ² g	1.02 ton	11	11.22
" at 6.3 kg/cm ² g	0.55 ton	8 credit	-(4.4)
" at 1.5 kg/cm ² g	0.64 ton	7 credit	-(4.48)
Cooling water	13 m ³	0.03	<u>0.39</u>
Total variable cost			
<u>Maintenance</u>			
3% of erected plant cost for materials and labour	1,204,110		12
<u>Operating Labour</u>			
9 operators x 3 shifts	= 27		
2 board supervisors x 3 shifts	= 6		
3 outside superv. x 3 shifts	= 9		
1 techn. director x 1 shift	= 1		
1 manager x 1 shift	= 1		
3 for contingencies x 3	= <u>9</u>		
	53		4.83

Input elements	Consumption ton/ton	Units price US\$	Cost of production per ton
<u>Overhead</u>			
150% of operating labour including administrative services and accounting staff			7.3
<u>Insurance and other expenses</u>			
0.5% of erected plant cost			2
<u>Depreciation</u>			
15 years			38
<u>Interest on Capital</u>			
10% of erected plant cost and interest on capital during construction			<u>45.3</u>
Cost of production of one metric ton cumene			480

Profitability and other economic parameters of cumene production

The economic analysis of cumene production indicates that the feedstocks cost (benzene and propylene) constitutes about 75% of the cost of production; and consequently the economy of cumene production is very much connected with the availability and prevailing prices of benzene and propylene. While the international market for both benzene and propylene is relatively active in demand and levels of prices, the cumene market tends to be stagnant and prices are below the average prices of 1985-1987 where the range was in the vicinity of 550 US\$ per metric ton.

Data published on aromatic compound prices during the years 1988 and 1989 indicate that cumene prices were depressed compared with the trends in its feedstocks prices (Table No. 15) *). The average prices for cumene for the

*) Several issues of Chemical Marketing Reporter, 1988, 1989

past 18 months range between 440-450 US\$ per ton.

Some cumene producers have stated that selling benzene (one of the main raw material for cumene) may be more interesting than the cumene which has a relatively low margin over benzene *). On the contrary, the phenol market is firm and prices range between 950 US\$ in USA to 1,100 US\$ in Western Europe **).

Table No. 15

Prevailing prices of cumene during 1988-1989

US\$/ metric ton

<u>1988</u>	<u>Price of Cumene US\$/ton</u>
March	440
May	436
July	469
September	408
September	440
November	443
December	374
<u>1989</u>	
January	384
February	458
June	440
July	440

Therefore, optimistic sale prices are not advisable to be adopted for the economic evaluation of a cumene project according to the historical and the prevailing rates. Consequently, this study had taken the safe side by considering the sales prices of cumene at 500 US\$ per ton representing the

*) Chemical Marketing Reporter, 12 December 1988

***) Chemical Marketing Reporter, 26 June 1989

average price of 1985-1989. Thus profitability and other economic parameters of the project have been calculated on this basis:

Production cost	48,000,000 US\$
Production value	52,800,000 US\$
(production cost + 10% ROI min.)	
Sales value	50,000,000 US\$
Return on investment	4.2%
Location	Iraq, Algeria, Egypt
Plant Site	10.000 m ²
Manpower	53-55

Plant Site and Manpower

The area allowed for a battery limits cumene plant is about 4,000 m² (90 m x 40 m). 150% of this area is also allowed for utilities and offsites facilities. Therefore, the total area required is about 10,000 m².

As for feedstock and product storages, these depend on the location and whether the cumene is for use directly in a phenol plant or for export.

If the cumene unit is located near by the benzene and propylene supply complex, then a storage tank of one day is usually enough; that is: 115 metric tons propylene and 198 metric tons benzene. If the feedstock source is located far from the cumene unit or to be imported, then storages for 1-2 weeks and 3-4 weeks operation (respectively) are necessary. The same case is applied for cumene product which usually does not require more than a surge tank or storage of one day if the cumene is sent directly to a phenol unit within the plant area or adjacent to it. However, if cumene is produced for export, then much larger facilities are required.

The manpower requirement for the operation of a cumene unit in the Arab Region was estimated at a total of 55 operators, supervisors and technical managers for the battery limits plant, utilities and offsites facilities (see Table No. 14).

CONCLUSIONS AND RECOMMENDATIONS

Based on the outcome of this study in regard to the availability of feedstock, the situation of the international market, capability of the Arab world market and the economic analysis, the following are concluded:

- 1) There is no certainty that the two main feedstocks (benzene and propylene) will be available at any one site in Arab countries. This condition is essential for cumene production economy.
- 2) The costs of feedstocks are relatively high as they occupy a firm market and are maintaining a good price level and profit margin.
- 3) On the contrary, cumene has been witnessing a sluggish market, stagnation and low sales prices.
- 4) Consumption of phenol (the ultimate product from cumene) in the Arab Region, presently and in the near and far future will not encourage a large cumene unit.
- 5) The production cost of cumene is relatively high due to the high prices of feedstock and the quantities required from the feedstocks to produce cumene (660 kg benzene and 380 kg propylene to produce one ton of cumene).

Therefore, unless a complete project of cumene/phenol/bisphenol A production is adopted within or adjacent to a petrochemical or refinery complex producing benzene and/or propylene, it is recommended that the phenol required for Arab industry be secured by import from the available international market.