EXECUTIVE SUMMARY

1.0 RELEVANCE OF DMF TO INDUSTRY

1.1 Dimethyl formamide (DMF) is an excellent solvent and finds major applications in acrylic fibre, PU processing, drugs and pharmaceuticals, dyes industries and other applications such as paints and pigment manufacture. DMF is a colourless, transparent, odourless, mobile and neutral liquid at room temperature, having a high boiling point. It is miscible with a wide range of organic as well as inorganic substances including water to be an excellent solvent of dipolar and aprotic nature.

DMF is stable even at its boiling point (153°C) under atmospheric pressure unless alkali, acid or a certain type of halogenated hydrocation coexists. Therefore, it can be distilled without causing any effect to its quality.

However, DMF will show thermal degradation at 350°C or higher temperature and form carbon monoxide and dimethylamine.

DMF may also show a photo chemical degradation by application of ultraviolet rays. When boiled in an aqueous solution, DMF will be hydrolyzed gradually to form formic acid and dimethylamine which are weakly acidic and basic respectively. Therefore, partial ionization will occur to show an increase in the electrical conductivity of the solution.

DMF forms stable complex compounds with HCl, SO_3, $POCl_3$, BF_3, heavy metal salts etc., under suitable conditions and they are used as catalysts. Caution should be exercised on DMF reactions with halogenated compounds, nitrates and chromic acids.

1.3 MANUFACTURING PROCESSES

Two processes dominate present-day commercial preparation of DMF :

1) Direct synthesis
2) Two step process

1.3.1 Direct Synthesis

The direct or one-step synthesis of DMF begins with either pure carbon monoxide or a gas stream containing carbon monoxide. This is reacted in a continuous process with N,N-dimethylamine (DMA), by using a solution of alkali alkoxide (usually sodium methoxide) in methanol as catalyst. Methyl formate is presumably formed as an intermediate. The reaction mixture passes over an external heat exchanger to remove the excess heat generated and to ensure thorough mixing of the components.

The reaction is conducted between 0.5 and 11 MPa at 50-200°C. The reaction mixture exits the reactor through a decompression chamber. In addition to N,N-dimethylformamide, the crude product contains methanol. A certain amount of acid or water deactivates any catalyst present resulting in the formation of sodium formate. Dissolved carbon monoxide, together with inert gases, escapes from the mixture during decompression and the off-gases are removed by combustion. Preliminary distillation is followed by second distillation in a separate column, here, dimethyl formamide is separated from methanol which contains traces of N, N-dimethylamine. Further distillation results in a product of 99.9% purity.

1.3.2 Two-Step Process

The two step process for the synthesis of N,N-dimethylformamide differs from direct synthesis because methyl formate is prepared separately and introduced in the form of 96% pure (commercial - grade) material. Equimolar amounts of methyl formate and N,N-dimethylamine are subjected to a continuous reaction at 60-100°C and 0.1 - 0.3 MPa. The resulting product is a mixture of N,N-dimethylformamide and methanol. The purification process involves distillation and is analogous to that described for direct synthesis. However, no separation of salts is required because no catalysts are involved in the process. Due to the corrosive properties of both starting materials and products, stainless steel has to be used as material of construction for production facilities.

2.0 INDIAN INDUSTRY STATUS

2.1 DMF Supply Scenario

Till late 1991, the country's entire DMF requirement was met through imports.

Presently, only RCF Ltd., has the capacity to produce DMF in India.

Their 2,500 TPA plant at Thal, based on technology from Acid Amine Technologies Inc., USA is likely to go into commercial production shortly. They are likely to double their capacity to 5,000 TPA by 1996. The decision to expand will be taken after the 2,500 TPA DMF plant is fully operational through the CO route.

Vam Organic Chemicals initiated work on a 3,000 TPA DMF project at Gajraula with technology from UCB, Belgium. They are planning only one step in this process. They will procure methyl formate from outside and react it with DMA to obtain DMF. The plant engineering is complete and is likely to go on stream shortly.

Alkyl Amines Chemicals Limited is also setting up a plant to manufacture 3,000 MT of DMAC/DMF.

There is no scope for additional capacity (in case RCF doubles their capacity to 5,000 TPA) till 1999-2000, considering a demand projection of around 7,400 tonne by 1999-2000.

2.2 DMF Demand Scenario

DMF finds its domestic end use in the following applications :

i) as a solvent in acrylic fibre production;

ii) in the manufacture of drugs and pharmaceuticals;

iii) in polyurethane (PU) processing and

iv) other miscellaneous application such as dyestuffs, paints, pigments etc.

Estimated percentage consumption by each end-use sector is given below.

Acrylic Fibre	44%
Drugs and Pharmaceuticals	38%
Polyurethane Processing	8%
Miscellaneous	10%
T O T A L ...	100%

DMF demand in India is expected to nearly double from the level of 2150 tonne in 1991-92 to 4100 tonne by 1995-96. The increase in demand is mainly due to upward trend in acrylic fibre production capacity.

3.0 INTERNATIONAL SCENARIO

3.1 Globally, DMF technology is licensed by only two companies one is Acid-Amine Technologies Inc. USA and the other is UCB. SA Belguim. Other global manufacturers - ICI,U.K., BASF, Germany, Air Products, U.S.A., and Dupont, U.S.A., are not interested in supplying or licensing technology or know-how for producing DMF.

The technology licensors are :

1) Acid - Amine Technologies Inc.
P.O. Box - 8733, Woodcliff Lake
New Jersey - NJ 07675
U.S.A.

They are involved in the business of technology transfer, complete process simulation and conceptual design, licensing of chemical production know-how, design of chemical plants, risk analysis, preparation of market, technical and feasibility studies and research studies in catalysts, membrane separations and distillation.

Plants available world wide are mainly based on the technology supplied by AAT, USA.

2) U.C.B. S.A.
Rue D Anderlecht 33
B 1620 Drogenbos
Belgium

They are involved in the manufacture of DMF with a total installed capacity of 15,000 TPA. Their process of manufacture involves the reaction of Dimethylamine and Methylformate. UCB S.A. has supplied technology to VAM Organics (India) Ltd.

3.2 Total installed capacity is estimated around 3 lakh tonne world wide compared to a total demand of about 1.8 lakh tonne (including captive use). There are 16 existing plants world wide. USA, Brazil and Canada share 24% of the total capacity, Europe (Germany, Spain, U.K., Belgium) share 38% of the total installed capacity, where as balance is shared by other countries.

Globally, demand is shrinking or atleast stagnant especially in Europe and America due to environmental reasons.

3.3 SALIENT FEATURES OF CONTEMPORARY TECHNOLOGIES

i) Acid-Amine Technologies Inc, USA

This technology involves the direct reaction of carbon monoxide (CO) and dimethyl amine (DMA) in the presence of sodium methylate in methanolic solution as a catalyst at an elevated temperature of 120°C and a pressure of 20 Kg/cm^2 in a gas loop reactor to produce dimethyl formamide (DMF), which is further purified to high quality solvent and fibre grade product. Solvent and excess dimethyl amine are fed back to the reactor and catalyst is removed continuously from the system. The process reaction is as follows :

$$(CH_3)_2\ HN + CO \xrightarrow[\text{Na methylate in methanolic solution}]{120^\circ C,\ 20\ Kg/cm^2} (CH_3)_2\ NCOH$$

Yield of DMF varies from 95% to 98%. Energy is required in the form of electricity as well as steam for heating. Requirement per tonne of DMF are as follows :

Steam - 0.85T/T of DMF
Electricity - 44 KWH/T of DMF
Environmental and Safety Aspects

The gaseous effluents in the form of inert gases and CO are flared through a flare stack system and get burnt when it comes in contact with the oxygen in the atmosphere. Thus pollution is kept under control.

ii) U.C.B. S.A., Belgium

In this process, methyl formate is first produced from carbon monoxide and methanol under high pressure and at 60-100°C temperature in the presence of sodium methylate. The methyl formate is distilled and then reacted with dimethylamine at 80-100°C and at a low pressure. The DMF is then purified and distilled.

The process reaction is as follows :

$$CO + CH_3OH \xrightarrow[\text{Na methylate}]{60\text{-}100^\circ C} HCOOCH_3\ (\text{methylformate})$$

$$HCOOCH_3 + (CH_3)_2NH \xrightarrow[\text{(DMF)}]{(80\text{-}100^\circ C)} HCON\ (CH_3)_2 + CH_3OH$$

Requirement per tonne of pure DMF are as follows :

Steam - 1.2 T/T of DMF

Electricity - 52 KWH/T of DMF

3.4 Technology Selection by Indian Companies

A. *RCF Ltd.*

1) There was no domestic manufacture of DMF till late 1991. Its entire requirements were met through imprts, presently around 2,500 TPA. Thus as an import substitution project, it was expected to save the country substantial foreign exchange of around 2.5 million dollars per year.

2) The company already had production of both di-methyl amine and carbon monoxide at its fertilizer plant. Given the fact that DMF uses these products as basic raw materials, the project was a good forward integration strategy.

   The project was also in keeping with RCF's corporate image as a leading public sector unit which is incidentally, the largest fertilizer and chemical company in Asia.

   RCF opted for AAT technology on the following counts :

   1) World-wide, AAT technology has greater acceptance than UCB, with the former accounting for more than60% of the global DMF installed capacity.

   2) RCF had earlier obtained AAT Technology for their existing methyl amines plant and were satisfied with AAT's technology and back-up services.

   3) AAT process used raw materials already available with RCF.

B) VAM Organic Chemicals Ltd.

They have opted for the technology from UCB, Belgium. Process uses dimethylamine and methyl formate instead of dimethyl amine and CO.

3.5 Comparative Evaluation of the Two Technologies

The project economics of UCB technology is less favourable to AAT technology even if DMA is produced at site as methanol is a byproduct in the case of the UCB technology which contains excess DMA or excess methylformate depending on the reaction conditions. This methanol has to be recycled either to methylamine plant or methyl formate plant. This leads to an increase in the number of process steps and therefore increase in the cost of production. It also leads to a setting up of a methylamine or methyl formate plant to improve the economics. Despite these investments, the overall economics cannot still be better than the AAT technology.

3.6 DEVELOPMENTS AT THE INTERNATIONAL LEVEL

Globally, Acid Amine Technologies Inc., USA is the only significant DMF technology licensor. Discussions held with Dr. Ian Williams, President AAT reveal that most R & D efforts at AAT concentrate on two aspects :

a) Catalyst improvement aimed at :

   1) Maximizing DMF yield

   2) Optimizing process parameters to control cost i.e. lower energy requirement per tonne of DMF.

b) Improving quality of input DMA to improve yield and purity of DMF.

UCB SA, Belgium had originally obtained Leonard/AAT process technology. Their plant has been operational for more than 20 years. They have reportedly modified/optimised the process to a level where by they are competent enough to license their technology.

Various patents have been registered by different firms to manufacture DMF, claiming better yields involving different raw materials. The following patents have been registered :

- Preparation of DMF from formamide & methanol with quarternary ammonium compound as a catalyst.
- DMF production by catalytic reaction of formamide and ethanol involving quarternary ammonium compound as a catalyst.
- DMF preparation from synthesis gas and ammonia or formamide in presence of platinum metal catalyst.
- Recovery of DMF by successive condensation of side fractions of the solvent vapour in the production of acrylonitrile and polyurethane filaments.

3.7 INTERNATIONAL COMPETITIVENESS OF THE INDIAN DMF INDUSTRY

With over capacities and shrinking/stagnant demand world wide, it is expected that fierce global competition will continue and this puts smaller DMF plants (like RCF and VAM Organics) into disadvantage. Higher prices of raw material inputs (dimethylamine, carbon monoxide, methyl formate) and poor economies of scale may result in higher cost of production. The international price of DMF is presently $ 880 / T (CIF Bombay). RCF's ex-works price is around Rs. 55,000/- per tonne. At this price it may not be able to compete with any global manufacturer. On the contrary, free imports may affect RCF and VAM Organics.

4.0 R&D EFFORTS, TECHNOLOGY ABSORPTION AND GAPS

4.1 R&D activities are carried out at AAT. Mainly research and development pertains to :

1) Catalyst improvement;
2) DMA Purity enhancement;
3) Overall reduction of production cost [mainly through (1) and (2)].

Some patents have been registered by various firms to manufacture DMF in order to reduce overall project cost and increase yields, involving different catalyst and cheaper raw materials than the present commercial process. Commercial economics of these processes however are yet to be evaluated.

4.2 Technology Absorption Efforts

RCF's DMF plant with CO as a raw material has still not been commissioned due to some problems in the CO separation plant for which know-how was obtained from M/s. KTI. This problem has now been largely overcome and the plant is expected to be commissioned through the CO route in the near future. Efforts for absorbing technology and making further improvements are only possible when the plant has been properly commissioned under the designed conditions.

RCF has a good track record in absorbing and updating imported technology. For example, improvements made in the methylamine plant at Trombay, which is based on the old Leonard Technology, was licensed to M/s. AAT for implementation in the plant supplied by them to their Turkish clients at fees US $ 30,000. Similarly, it is expected that absorption and updation of DMF technology is very much within the capabilities of RCF after the plant is commissioned.

4.3 TECHNOLOGY GAPS/THRUST AREAS

a) Product

As mentioned earlier RCF has collaborated with AAT. The product obtained on trial runs is meeting the international specifications/ standards and the grades available are either as 99.9% solution or 100% anhydrous. In order to utilize the above solvent, one should keep abreast of developments of AAT in order to maintain international standards and develop it accordingly for the specific end-use grade in the Indian context.

b) Raw Materials

Basic raw material required to manufacture DMF by AAT technology are Dimethylamine and Carbon monoxide. DMA plant facilities at RCF have been setup in collaboration with AAT, USA, hence the DMA specifications/standards meet international standards. CO is recovered with Cosorb solvent imported from M/s. KTI, USA. However, requirement of this solvent is only about 10 m^3 every four years depending on the proper operation of the plant and degradation of the solvent.

c) Utilities

Utilities are mainly in terms of electricity, steam and water. RCF's plant is yet not on full stream, hence rated requirement of power, steam and water has to be verified once the plant is at the peak level of production.

d) Capital Equipments

Instruments like DDCS were obtained from Instrumentation Ltd, where as instruments like CO meters were imported, which need to be developed indigenously.

e) Safety

Enough care has been taken to control pollution by employing flare stack system and various other measures are taken to control adverse environmental effects by adhering to good manufacturing practices.

f) Training

Under the collaboration agreement signed between RCF and AAT, four RCF personnel were trained at AAT, USA. RCF may be developed to the status where its DMF plant can be a training center for South

Asian nations adopting AAT technology, hence earning foreign exchange.

g) Application

DMF is mainly used as a solvent in the acrylic fibre manufacture and PU processing. RCF should initiate more interaction with end-users in India and try to tap export potential as our product is expected to meet international standards.

5.0 RECOMMENDATIONS

5.1 Technology Acquisition

Foreign collaboration for technology acquisition may be allowed for time being. Once the requisite technologies have been absorbed, the need for technology collaboration may cease except in certain areas where specific equipment imports will have to be made.

5.2 Technology Development

An alternative route can be explored to obtain DMF. For example the patented process of DuPont involves the reaction of formamide and methanol to produce DMF. This process is claimed to give better yield and lower cost of production per unit production of DMF. Research work in this direction can be initiated in a joint collaborative effort by NCL, Pune and RCF, Bombay.

5.3 Applications

New application development projects may be taken up by RCF. One of the areas could be more usage in the drugs and pharmaceutical industry as an extracting solvent. Existing end-users can also help in developing the product in the Indian context to meet new applications.

5.4 Capital Equipment Indigenisation

While sufficient expertise is available for fabrication of equipments like vessels and heat exchangers, capabilities of vendors for proper design of package units like gas dryers and low temperature chilling plants are limited. Detailed engineering contractors may properly evaluate such designs and advise the vendors in the overall interest of indigenisation.

5.5 Product Cost

Efforts may be made to improve the process in order to bring down the cost of production to make it competetive with the imported product.