

CHAPTER ONE

1.1 Overview on Acrylic Acid Technology

Petrochemicals are derived from crude petroleum oil and natural gas. The typical feedstocks are natural gas, natural gas liquids (NGL), naphtha, and gas oil and refinery gases. These products come from crude oil and natural gas. Crude oil is processed into naphtha, gas oil and refinery gas streams. NGLs (ethane, propane, butane) are separated from natural gas. These feedstocks for petrochemical processing are fed into reactors. Through the application of heat and pressure or by reaction with other raw materials, they are converted into primary petrochemicals methanol, olefins and aromatic, which are then separated by distillation and extraction. Most primary petrochemicals are further processed and upgraded. Petrochemical intermediates are generally produced by chemical conversion of primary petrochemicals to form more complicated derivative products. Petrochemical derivative products can be made in a variety of ways: directly from primary petrochemicals; through intermediate products which still contain only carbon and hydrogen; and, through intermediates which incorporate chlorine, nitrogen or oxygen in the finished derivative. In some cases, they are finished products; in others, more steps are needed to arrive at the desired composition. Of all the processes used, one of the most important is polymerization. It is used in the production of plastics, fibers and synthetic rubber, the main finished petrochemical derivatives (Figure 1.1) [1].

Malaysia has the 25th largest crude oil reserves and the 14th largest gas reserves in the world. Combined, Malaysia has total reserves of 18.82 billion barrels of oil equivalent (boe): 82% gas and 18% oil. Average oil production is around 600,000 barrels per day. Average natural gas production stands at approximately 5.7 billion

standard cubic feet per day. At the current rates of production, Malaysia's oil and gas reserves are expected to last for another 17 and 34 years, respectively. While Malaysia is currently a net exporter of crude oil, the country is expected to become a net importer of crude oil around 2005/06 [2] (Table 1.1).

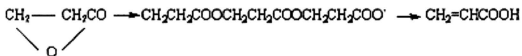
The upgrading of component in natural gas such as propane has gained importance as a raw material for an array of chemicals such as acrolein, acrylonitrile, acrylamides and in particular, acrylic acid. The world acrylic acid and derivatives industries are concentrated with seven major players: BASF, Rohm & Haas, Celanese, Nippon Shokubai, Union Carbide, StoHaas and American Acryl (Figure 1.2) [3, 4 and 5]. Today the major industrial process to produce acrylic acid is by gas-phase catalytic oxidation of propylene. Roughly three-quarters of its production is converted directly into acrylate esters and the rest is purified into glacial acrylic acid. The commercial process used worldwide for making acrylic acid via two-step process [6]. This process was first developed by Distillers, and later followed by BASF, Sohio, Toyo Soda, Union Carbide, Nippon Shokubai, Rohm Haas, etc [7]. This process starts with propylene and goes through acrolein as the intermediate to make acrylic acid. Alternatively, acrylic acid can also be produced from a one-step oxidation of propane in gas phase with molecular oxygen to acrylic acid [8] (Figure 1.3). This catalyses reaction, which involved the transfer of eight electrons, most likely requires the coordinated effort of several active sites, as well as balanced reduction-oxidation properties of the catalyst to complete the catalytic cycle. Compare to the propylene oxidative dehydrogenation, this reaction required the transfer of more electron or oxygen atoms. In terms of product stability, acrylic acid, the desired product in propane oxidation, is less stable and more prone to further oxidation than acrylonitrile and maleic anhydride, the desired product in propane ammoxidation and *n*-butane oxidation respectively. Part of the instability of acrylic acid is likely to be related to the

additional adsorptive ability of its acid functional group onto the catalyst surface, which renders it susceptible to further oxidation. Overall, there has been a perception that it is very difficult to achieve a high acrylic acid yield in a one-step propane oxidation [6, 9], but converting to an abundant fuel into a high valuable chemical feed stock, propane less expensive than propylene and this extensive effort to replace the propylene to propane. There are few methods to produce acrylic acid that have led to industrial plants or to extensive pilot development [1]:

- Hydrolysis of ethylene cyanohydrin:** This process involves the acidic hydrolysis and dehydration of ethylene cyanohydrin (from ethylene oxide and hydrogen cyanide) and the removal of the product from the reaction mixture by distillation. Like all other preparation of polymerisable monomers, care must be exercised to remove the product from the reaction mixture and either inhibits or appropriately cool it before uncontrolled polymerization can occur.

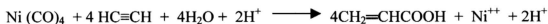


- Polymerization of β -propiolactone:** This commercial method is based on the polymerization of propiolactone and the destructive distillation of this polymer to form acrylic acid.



- Oxidative carbonylation of ethylene:** Basic raw materials in the preparation of acrylic acid by the carbonyl reaction are acetylene carbon monoxide (supplied as such or in the form of nickel carbonyl), and water. Three distinct methods are known.

Stoichiometric Carbonyl Reaction: The reaction is very rapid at atmospheric pressure and at mild temperature. The hydrogen shown in the accompanying equation does not appear in gaseous form but is consumed by side reactions



Catalytic Carbonyl reaction: The catalytic reaction requires elevated temperature and super atmospheric pressures. Nickel salts or complexes thereof are used as catalysts.



Semicatalytic Carbonyl Reaction: The catalytic reaction (nickel carbonyl) of acetylene, carbon monoxide and water is superimposed upon the stoichiometric reaction of nickel carbonyl, acetylene, water and acid. In this way the very mild conditions characteristic of the stoichiometric reaction can be used, with a large proportion of the total CO being supplied as carbon monoxide gas, the remainder being supplied in the form of nickel carbonyl.

- **Acrylonitrile Method:** Care must be exercised in this acid hydrolysis since both the starting acrylonitrile and the product acrylic acid are polymerisable. The acrylonitrile should remain in the reaction zone and, hence, must be well inhibited. A major advantage of this method is the increase in molecular weight on hydrolysis from 53 to 72, which provides a definite yield improvement.



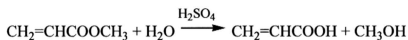
- **Propylene Method:** This recently developed process involves the oxidation of propylene to hydroxypropionic acid: oxides of nitrogen or nitric acid act as catalyst

for the reaction. Subsequent dehydration yields acrylic acid. The stepwise representation can be shown as follows:

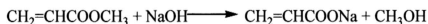


An alternative route is the catalytic oxidation to acrolein, CH_2CHCHO , and then to acrylic acid with oxygen and certain metallic catalyst such as Mo, Co, or Ce.

- **Acrylic Ester Method:** This method is hampered by the ready polymerisability of the starting material, and the low boiling points of the most available esters and the formed alcohols as compared with that of the product, acrylic acid.



It is generally preferable to saponify the ester to form the corresponding salt.

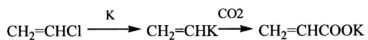


The salt can then be converted to the acid by: Neutralizing the calcium salt with sulphuric acid, removing precipitated calcium sulfate by a difficult filtration procedure, and obtaining the formed acrylic acid in aqueous concentrate. Treating an aqueous solution of sodium salt with ion-exchange resin to remove sodium ions, removing the resin by filtration, and obtaining an aqueous concentrate of acrylic acid.

- **Maleic Acid Method:** This patented method involves the decarboxylation of maleic acid to form the desired acrylic acid

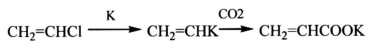


- **Potassium Vinyl Method :** The low temperature conversion of vinyl chloride with potassium metal and a subsequent treatment of the cold vinyl potassium with dry ice are reported to give potassium acrylate in 70% conversion. Customary methods produce acrylic acid.



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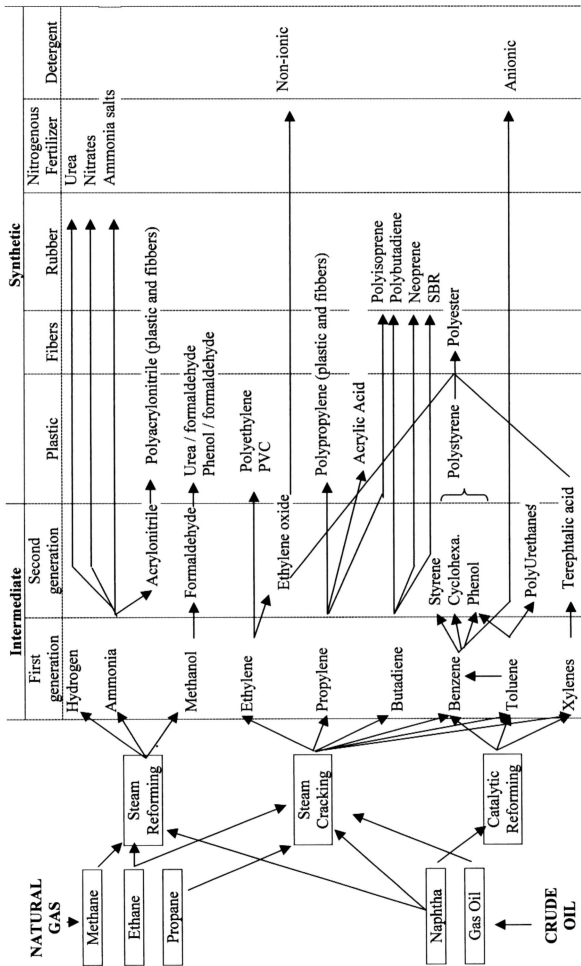


Figure 1.1 Overview of petrochemical intermediates manufactures [1].

Table 1.1: Asia Crude Oil and Natural Gas Reserves, January 1, 2002 (Important Note on Sources of Foreign Reserve Estimates)

Region/Country	Crude Oil (Billion Barrels)	Crude Oil (Billion Barrels)	Natural Gas (Trillion Cubic Feet)	Natural Gas (Trillion Cubic Feet)
	Oil and Gas Journal ¹	World Oil ²	Oil and Gas Journal ¹	World Oil ²
Asia & Oceania				
Afghanistan	0.0	0.0	3.5	0.0
Australia	3.5	3.8	90.0	80.0
Bangladesh	0.1	0.0	10.6	0.0
Brunei	1.4	1.2	13.8	8.5
Burma	0.1	0.2	10.0	12.2
China	24.0	29.5	48.3	42.8
India	4.8	3.8	22.9	15.4
Indonesia	5.0	9.2	92.5	87.5
Japan	0.1	0.0	1.4	0.0
Malaysia	3.0	4.5	75.0	82.5
New Zealand	0.1	0.1	2.1	2.1
Pakistan	0.3	0.3	25.1	24.1
Papua New Guinea	0.2	0.5	12.2	15.0
Philippines	0.2	0.2	3.7	3.7
Taiwan	0.0	0.0	2.7	0.0
Thailand	0.5	0.6	12.7	13.3
Vietnam	0.6	2.2	6.8	6.8
Other	0.0	0.6	0.0	26.1
Total	43.8	56.5	433.3	419.9
World Total	1,032.0	1,018.7	5,457.1	5,930.2

Source:¹³ PennWell Publishing Co., *Oil & Gas Journal*, Vol. 99, No. 52 (December 24, 2001)

¹⁴ Gulf Publishing Co., *World Oil*, Vol. 223, No. 8 (August 2002).

¹⁵ Data for the United States are from the Energy Information Administration, U.S.

Crude Oil, Natural Gas, and Natural Gas Liquids Reserves, 2001 Annual Report, DOE/EIA-0216 (2001) (November 2002).

Includes one-half of the reserves in the Neutral Zone.

1.2 Application of Acrylic Acid

Acrylic acid is versatile unsaturated carboxylic acid. It can react further with a large number of organic and inorganic compounds and intermediates for the synthesis of many low and high molecular weight compounds. Some typical reaction/application includes:

- Copolymers with acrylic esters, methacrylic esters, acrylonitrile, maleic acid esters, vinyl acetate, vinyl chloride, styrene, butadiene and ethylene. Methacrylic is used to produce acrylic fiber for surface coating and textile industry. Ethyl acetate is used primarily as an intermediate in the production of emulsion-based polymers.
- Homopolymers of acrylic acid and copolymers form water-soluble compound in acid form or their alkali/ammonium salts. Uses included thickening agent, dispersing agent, and protective colloid for stabilizing emulsions and polymers dispersion wetting agents.
- Super absorbent polymer is lightly cross-link polyacrylic acid salt. They are used for fluid retention largely in baby diapers, but also in products for feminine hygiene, adult incontinence and agriculture.
- Copolymers with less than 50% acrylic acid produce polymers only slightly soluble or even insoluble in water. Their alkali or ammonium salt are used in sized, adhesive intermediate, and binder for printing inks and coatings.

As a vinyl compound in addition acid-acrylic esters, acrylamide, n-substitute amides and acrylic acid chloride.

1.3 Acrylic Acid Market and Demand

Global acrylic acid market is balance, as steady demand in the USA and Europe absorbs overcapacity in Asia (Figure 1.4) [10]. The current market demand of acrylic acid is over 1 million tons, which is growing by 5% per annum. Some 75% of production is converted into acrylate esters and the rest is purified into glacial acrylic acid. Historically, prices of glacial acrylic acid have varied between \$1400 and \$1900 per ton. The growing demand for absorbent polymers in emerging economies is the main driver of the growing market of acrylic acids [11].

The main applications of acrylic acid are polyacrylic acids (e.g. super absorbent polymers, detergent, water treatment and dispersant) (35%), n-butyl acrylate (30%), ethyl acrylate (20%), methyl and 2-ethylhexyl acrylate (7%) and specialty acrylates (5%). Super absorbent polymers are the fastest growing market for acrylic acids (e.g. for hygiene paper and nappies). The market for commodity acrylic acids is closely tied to coating, a mature market. The players in the acrylic acid market are as shown in Table 1.2 [12].

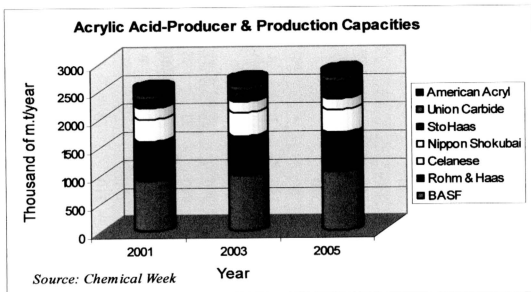


Figure 1.2: Acrylic Acid producer & production capacities [3].

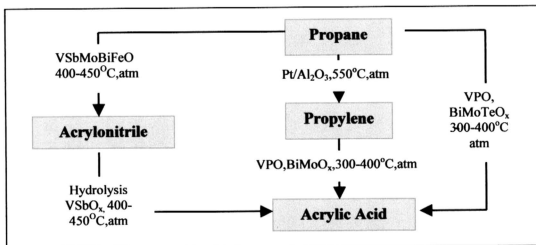


Figure 1.3: Acrylic Acid route [7].

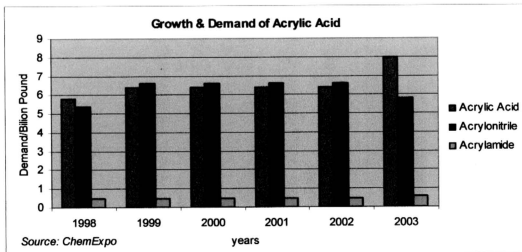


Figure 1.4: Worldwide Demand of Acrylic Acid [3].

TABLE 1.2: Production Capacities and Market Share of worldwide [11,12 & 16].

Producers	Location	Prod. Cap. In thsn (m.t/yr)				Market Share (%)	
		1999	2001	2003	1999	2001	2003
BASF	Freeport, TX U.S	300	220	500	19	9	12
	BASF-Petrobras, Guaratinguet, Brazil		160	160		6	4
	Antwerp, Belgium		190	190		7	5
	Ludwigshafen, Germany	310	310	310	19	12	8
	BASF-Yangzi, Nanjing China			160			4
Rohm & Haas	BASF-Petronas, Kuantan, Malaysia		160	160		6	4
	Total	610	1040	1480	38	40	37
Celanese	Deer Park, TX U.S	517	575	650	32	22	16
	Clear Lake, TX U.S	272	290	360	17	11	9
Dow Chemical	Cangrejera, Mexico			65			2
	Total	272	290	425	17	11	11
American Acryl	Taft, LA, U.S	110	110	110	7	4	3
	Pasadena, TX, U.S		120	120		5	3
Oxiqumica	Carling, France			240			6
	Triunfo, Brazil			66			2
StoHaas	Marl, Germany		165	165		6	4
	Bohlen, Germany		80	80		3	2
Nippon Shokubai	Himeji, Japan			220			5
	Yokkaichi, Japan		110	158		4	4
LG Chemical	Cilegon, Indonesia		60	60		2	1
	Naju, South Korea			95			2
Formosa Plastics	Miliao, Taiwan			60			1
	Linyuan, Taiwan			55			1
Sumika Glacial Acrylic Pte. Ltd	Pulau Sakra, Singapore	60	60	60	4	2	1
	Singapore	25	25	25	2	0.9	0.6
TOTAL		1594	2635	4069	100	99.9	99.6

1.4 Aims of study

The scope of work includes;

- a). To synthesis unpromoted and promoted $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}$ oxide catalysts system via different preparation method and activation procedure for selective oxidation process.
- b). To characterise unpromoted and promoted $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}$ oxide catalysts by various technique, such as surface area analysis by BET, Scanning Electron Microscope-EDX (SEM-EDX), Powder X-ray diffraction (XRD), Temperature-Programmed-Reduction (TPR), Thermo gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) to optimised the performance of the catalyst.
- c). To optimise the performance of unpromoted and promoted $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}$ oxide catalysts system.

The objective of this study is to optimise the synthesis and activation of promoted and unpromoted $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.12}\text{O}_x$ catalyst system.