

**POLYURETHANE
CHEMICALS
IN
ALBERTA**

**prepared for
ALBERTA ECONOMIC DEVELOPMENT**

by

T. J. McCann and Associates Ltd.
and
Sigurdson & Associates

December 2001

DISCLAIMER

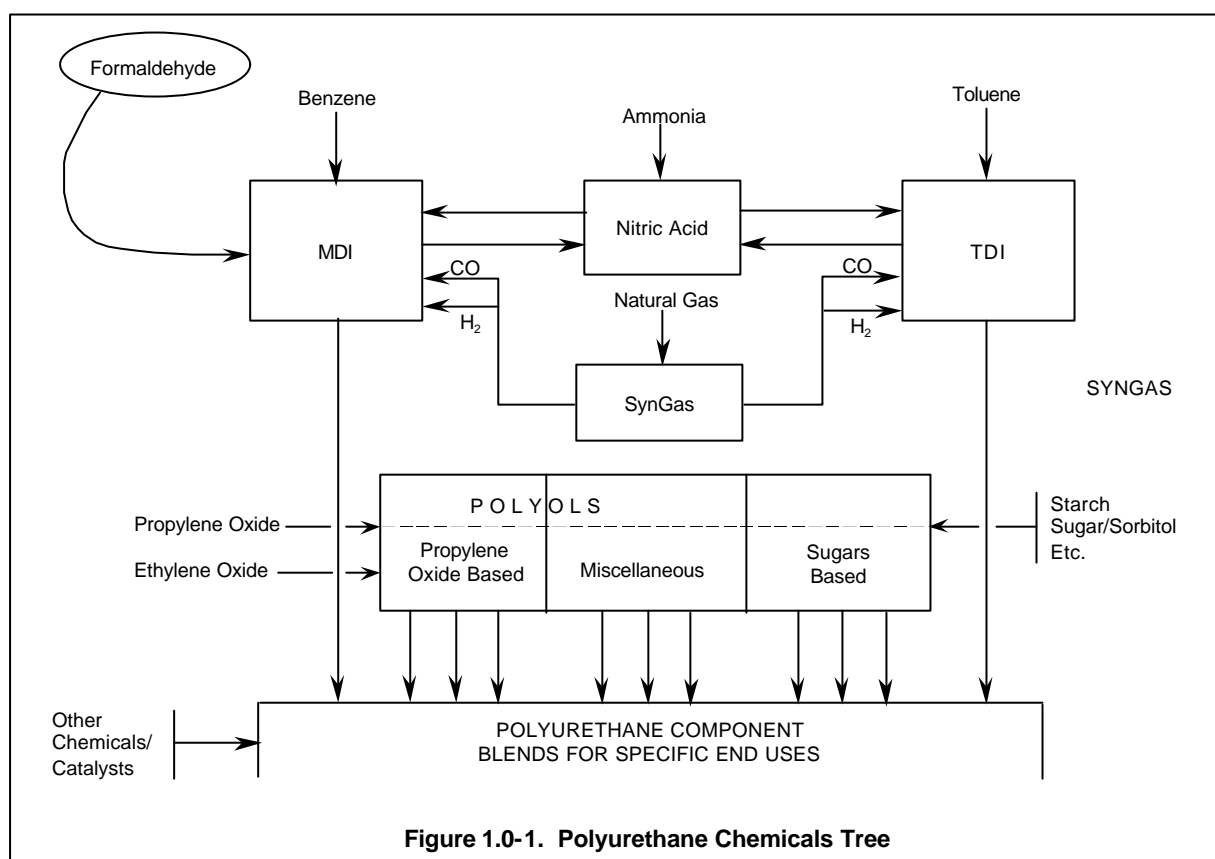
The report is the sole responsibility of the authors and its data; conclusion and/or recommendations may or may not agree with the policies or understanding of Alberta Economic Development.

TABLE OF CONTENTS

	PAGE
DISCLAIMER	i
1.0 EXECUTIVE SUMMARY	1
2.0 INTRODUCTION	3
2.1 Polyurethane Chemicals and Coverage.....	3
3.0 POLYURETHANE APPLICATIONS	5
3.1 Major Urethane Chemicals.....	7
3.2 Toluene Di-isocyanate (TDI)	8
3.2.1 TDI Producers.....	8
3.2.2 Outlook for TDI.....	10
3.2.3 Regional use of TDI	11
3.2.4 Technology Change in TDI Applications	11
3.3 Methyl Di-isocyanate.....	12
3.3.1 MDI Producers.....	12
3.3.2 Outlook for MDI.....	13
3.3.3 Regional Use of MDI	14
3.3.4 Technology Change in MDI Applications	16
3.4 Aniline and Nitrobenzene	17
3.4.1 Aniline Producers.....	17
3.4.2 Nitrobenzene Producers	18
3.4.3 Outlook for Aniline and Nitrobenzene Regionally	19
3.5 Urethane Polyols.....	19
3.5.1 Polyol Producers.....	20
3.5.2 Outlook for Urethane Polyols	21
3.5.3 Regional Use of Urethane Polyols	21
3.5.4 Technology Change in Polyol Applications	21
3.6 Propylene Oxide	22
3.6.1 Propylene Oxide Producers.....	22
3.6.2 Outlook for Propylene Oxide.....	23
3.6.3 Regional Use of Propylene Oxide.....	23
3.6.4 Technology Change in Propylene Oxide Applications	24
3.7 Sorbitol.....	25
3.7.1 Sorbitol Producers	25
3.7.2 Outlook for Sorbitol.....	26
3.7.3 Regional Use of Sorbitol	26
4.0 ISOCYANATES	28
4.1 Introduction	28
4.2 Material Balances and Process Modules	28
4.3 Feedstock Availability	31
4.4 Process Review	32
4.4.1 General.....	32
4.4.2 Nitration and Related Acid Systems.....	32
4.4.3 Nitric Acid.....	32
4.4.4 Aniline.....	33
4.4.5 Toluene Diamine.....	33
4.4.6 MDI Diphenyl Urea/Ethyl Phenyl Carbamate/MDN/and Cracking	33
4.4.7 CO and Hydrogen.....	34
4.4.8 TDA Carbonylation and Cracking.....	34
4.5 Environmental Considerations.....	34
4.6 PHOSGENE ROUTES TO DI-ISOCYANATES	37
4.7 MDI/TDI Complex Costs and Operations.....	38
5.0 POLYOL PRODUCTION	40
5.1 Introduction.....	40
5.2 Propylene and Ethylene Oxides.....	41
5.2.1 Ethylene Oxide and Glycols.....	41
5.2.2 Propylene Oxide and Glycols.....	42
5.3 Polyol Production.....	44
6.0 SUMMARY	46
6.1 General.....	46
6.2 Isocyanate Production.....	47
6.2.1 MDI Production.....	47
6.2.2 TDI Production in Alberta.....	47
6.2.3 Phosgene Route to Isocyanates?.....	48
6.3 Propylene Oxide/Ethylene Oxide	48
6.3.1 Propylene Oxide Production	48
6.3.2 Ethylene Oxide.....	48
6.4 Polyol Production in Alberta.....	49
REFERENCES	50

1.0 EXECUTIVE SUMMARY

Polyurethane use is expanding in North America at a rate of approximately 5 to 7% for MDI – methylene di-isocyanate – based products and about 5 to 6% for those based on TDI – toluene di-isocyanate. North American polyurethane demand is in the order of 3,000-kilotonnes a year. Generally, MDI and TDI products serve different markets – MDI oriented towards many market sectors and TDI towards less extensive markets.



This study concentrated on the large volume ingredients going into polyurethane manufacture – the two principal isocyanates, polyols (generically) and their principal oxide feeds – with the small-scale isocyanates catalysts, surfactants and blowing agents largely neglected as very small-scale and except for blowing agents, without any major economic ties to feedstocks and low-cost utilities. The di-isocyanates constitute only 30 to 70% of any specific polyurethane product, the rest being polyols – selected sugar alcohol like chemicals that bind to the isocyanates to produce flexible and rigid foams and many polyurethane products.

Analysis indicates an Alberta 100-ktpa MDI plant should be attractive at or close to world scale. A smaller TDI plant – say 50-KTA – can be considered, as an adjunct to an MDI facility. While there are major production synergies TDI product potential is not as well identified as is that for MDI.

MDI would be produced from benzene, ammonia, formaldehyde and natural gas, all but the benzene readily available today in Alberta. Benzene supply potential was noted in a prior study, appearing to need major new markets here before proceeding. TDI would require toluene, which would come from such a new benzene source facility. The MDI and TDI facilities would be somewhat similar to the smaller-scale petrochemical units at the Celanese Edmonton plant site – smaller scale, but with higher unit production values than most Alberta petrochemical plants.

Most polyols build on propylene oxide, which could be produced here from hydrogen peroxide and propylene or in conjunction with a major new benzene derivative – styrene – facility. Ethylene oxide, an intermediate in the production of ethylene glycols at two Alberta locations, is another prospective base stock. These oxides are reacted with a variety of sugar forms or derivatives, and other chemicals to form the many polyols needed across the polyurethane, food and other polyol markets appears another ideal “new” Alberta industry. The final production here of various polyols is not critical, as the specific urethane chemical “mixes” could be prepared at a variety of dispersed sites near regional markets.

The final stages of MDI and TDI production use proprietary process technologies to be brought with the project developers. For example, Dow Chemical is quite active internationally in urethane chemical production and marketing worldwide and have the appropriate technologies and interests. Propylene oxide is also an interest at each of these and the European branch of another local chemical plant operator has recently proved up a hydrogen peroxide plus propylene route to propylene oxide. BASF has just announced a NAFTA or European project, based on the same feedstocks. There is active interest in Alberta starch to sucrose conversion.

A polyurethane chemical industry in Alberta would significantly extend the breadth of chemical production.

2.0 INTRODUCTION

This study on the potential for production in Alberta of significant chemicals going into polyurethane products was commissioned by Alberta Economic Development. The study considers chemicals considered most likely to lead to a polyurethane ingredient industry in Alberta. The study is intended to provide bases for consideration and promotion of the production of such chemicals in Alberta. It will be noted later that very proprietary technologies are involved in a few key processing steps, processes that will come with the plant operator.

Polyurethane chemical production goes back many years, but with advances in polyurethane technologies there are changing patterns of demands for specific chemicals.

Various Alberta represented chemical companies such as Dow Chemical and Shell Chemicals are prominent in certain areas of polyurethane chemical supply. But Alberta currently has little equivalent scale/value-added and polyurethane chemicals production here would be an ideal fit in our very large scale basic petrochemicals oriented scene supplying polyurethane chemicals globally.

2.1 Polyurethane Chemicals and Coverage

“Polyurethane products are produced by the reaction of a di-isocyanate “side” (e.g., MDI or TDI) and a blended polyol “side” consisting typically of a polyol, an amine and/or metallic salt catalyst, a silicone surfactant and for polyurethane foams, a blowing agent.”¹ A wide variety of dispersed compounds provide such a basket of chemicals to the polyurethane producer.

The primary polyurethane polymerization reaction is as follows:



where R contains one or more benzene rings and R' is generally paraffinic in nature.

The polyol usually contains 3 to 8 HO groups.

While there are only two major (and 10 to 12 minor) isocyanates, there are an infinite variety of polyols to provide the flexibility/rigidity and other properties needed in specific urethane polymers. However, as will be seen, propylene oxide is often a major ingredient in polyol production.

This study concentrated first on the di-isocyanates – in particular PMDI² - a blend of MDI and MDI polymers – and TDI, toluene di-isocyanate, which in total represents well over 90% of di-isocyanates used in polyurethanes. The production of polyol chemicals is considered in three parts – the production of propylene oxide (and to a lesser extent ethylene oxide), the supply of molecules with many – OH (hydroxy) groups and the catalyzed reaction of the oxide and hydroxy-rich compounds into a polyol.

The final actual polyurethane production is very specific to each manufacturer. The smaller-scale chemicals noted above – catalyst and surfactants – and blowing agents are not covered here, their manufacture being small-scale at a few specialty chemical plants. Such plants are “footloose” being located only where the owner prefers, whereas with the isocyanates and oxide and to a limited extent hydroxy compounds, feedstock supply and utility supply are important.

¹ From Technical Bulletin of Alliance for the Polyurethane Industry.

² The P denoting a mix of pure MDI and its polymers is usually dropped (but small quantities of pure MDI are made).

3.0 POLYURETHANE APPLICATIONS

Urethane chemistry's flexibility in being able to provide various properties to articles has spread applications throughout modern society. Market use runs from flexible cushion foam and rigid insulation through to Spandex fibers and specialty adhesives.

Table 3.0-1. Market Size of Urethane Applications, 1998 <i>(in US & Canada)</i>		
Market	Volume <i>(million kg)</i>	Percent Total
Flexible foams	847.2	32
Molded flexible	270.6	10
Rigid foams	683.3	25
Coatings	242.4	9
Binders	182.5	7
Elastomers	103.1	4
Adhesives	100.3	4
RIM	75.8	3
Sealants	74.9	3
Thermoplastic Urethanes	38.6	2
Fibers	25.4	1
TOTAL	2644.1	100
Source: Alliance for Polyurethane Industry study, 1999		

The applications in the table above involve the reaction of a polyol and an isocyanate along with fillers, catalysts, foaming agents, fillers, pigments, flow promoters, and other additives. The binder application is involved with the foundry industry and the strand board (OSB) sector of wood products. These applications tend to use PMDI alone for binding wood chips or sand for the product or production process.

Overall, growth in polyurethane applications has been running in the 33.5% annual level with slightly greater growth in Canada. The swing to isocyanate binders in the OSB industry along with a fairly strong auto parts business has helped to cause the demand increase.

Table 3.0-2. Urethane Chemistry in Summary

- Polyurethanes are formed by reacting a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a di-isocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives
- Because a variety of di-isocyanates and a wide range of polyols can be used to produce polyurethane, a broad spectrum of materials can be produced to meet the needs of specific applications
- Most polyurethanes are thermoset materials; they cannot be melted and reshaped as thermoplastic materials can be
- Polyurethanes exist in a variety of forms including flexible foams, rigid foams, chemical-resistant coatings, specialty adhesives and sealants, and elastomers
- Rigid polyurethane foams are used as insulation for buildings, water heaters, refrigerated transport and commercial and residential refrigeration. These foams are also used for floatation and for energy management
- Flexible polyurethane foams are used as cushioning for carpet and in upholstered furniture, mattresses, and automobiles. These are also used for packaging
- Polyurethane adhesives and sealants are used in construction, transportation, marine and other applications where their high strength, moisture resistance and durability are required
- The term 'polyurethane elastomers' includes such diverse products as thermoplastic polyurethanes, cast elastomers and Reaction Injection Molded (RIM) products. These materials go into a wide variety of applications from footwear and skate wheels to machinery housings, to athletic tracks to electronic media

Source: Alliance for the Polyurethanes Industry

The flexible urethane products are dominated by polyol and toluene di-isocyanate reactions, usually producing an open-cell foam. The flexible polyurethane business in Canada and the US supplies major volumes to the automotive industry – both for molded seats as well as interior padding, including dashboards. The interior of homes and offices is the other major market area where flexible urethane foam provides carpet underlay and furniture cushioning.

Table 3.0-3. Application Structure of North American Flexible Urethanes Market, 1998

Market	Volume (million kg)	Percent (%)
Carpet cushion	227.5	23
Furniture	204.8	20
Auto interior	363.7	36
Transportation molded	188.0	19
Other flexible	25.0	2
TOTAL	1009.0	100

Rigid foams have both excellent insulative properties, as well as semi-structural and adhesive characteristics. As a result, construction insulation – both board and spray-on urethane – is a major application area. Appliance use lies in the refrigeration and consumer refrigerator appliance production, while tanks and pipes are covered with urethane foam to provide insulation. Furniture decorations, marine buoyancy and insulation, as well as highway trailer, travel trailer, truck and specialty equipment use urethane foams for stiffening and insulation in their designs.

Market	Volume (million kg)	Percent (%)
Construction	388.6	57
Appliances	124.9	18
Packaging, tanks, pipes, transportation & marine	169.8	25
TOTAL	683.3	100

3.1 Major Urethane Chemicals

Urethane chemistry involves an –OH donor and an isocyanate, which react to form a polymer. However, the wide applicability of urethane chemistry means that modifiers, catalysts, blowing agents, extenders, flow control modifiers, and a host of other chemicals are used to refine the basic urethane chemicals for a particular application, or to allow for the processing of the urethane chemicals in production machinery. In this analysis, the emphasis is on the basic urethane chemicals – polyols and isocyanates.

Chemicals of Focus in the Study

- Toluene di-isocyanate
- MDI methyl di-isocyanate
- Polyols (polyester & polyether)

There are also several intermediate chemical required to make these urethane chemicals. From an investment, potential analytical point of view there is also a need to examine the raw materials for making these chemicals and the potential for the intermediates to be manufactured in Alberta.

Intermediate Chemicals for Urethanes in the Study

- Aniline
- Nitrobenzene
- Propylene oxide
- Sorbitol

3.2 Toluene Di-isocyanate (TDI)

Toluene di-isocyanate is one half of the monomer system used to make flexible urethane foams. In addition, it goes into some coatings and elastomers. In comparison with MDI, it is the more mature product and has been experiencing lower growth in the past few years. However, TDI is facing a capacity short-fall in the coming years both in North Americas well as in the world generally due to the lack of investment in this product area by the urethane chemical producers.

3.2.1 TDI Producers

The global capacity for TDI was 1,680 Ktonnes in 2000 with about 30% of that capacity in North America. Mexico has one small plant. There is a plant in West Virginia and the balance of capacity is located in Texas and Louisiana.

Table 3.2.1-1. Producers of TDI in North America (Ktonnes/yr.)	
Producers	Capacity
BASF, Geismar, LA	116
Bayer, Baytown, TX	70
Bayer, New Martinsville, W.VA.	50
Dow, Freeport, TX	65
Huntsman/ICI, Geismar, LA	35
Lyondell, Lake Charles, LA	136
Cydsa-Bayer, Cotzacolcos, Mexico	17
TOTAL	489

From a raw material point of view Dow and Lyondell/Bayer are integrated into toluene, while the other producers buy on a merchant basis. Interestingly Dow produces its toluene in Louisiana, while Lyondell makes toluene in Texas.

Table 3.2.1-2. TDI Plants on a Global Basis	
Plant	Capacity (Ktonnes/yr.)
Europe	
Bayer, Brunsbuttel, Germany	66
Bayer, Dormagen, Germany	60
Bayer, Leverkusen, Germany	36
Lyondell-Rhone Poulenc, Pont de Claix, France	70
Lyondell-Rhone Poulenc, Lille, France	45
Bayer/Shell, Antwerp, Belgium	30
EniChem, Porto Marghera, Italy	120
Bayer, Tarragona, Spain	341
Asia	
Nippon Polyurethan, Shin Nanyo, Japan	19
Sumitomo-Bayer, Niihama, Japan	13
Kyodo TDI, Omuta, Japan	27
Mitsui, Omuta, Japan	67
Takeda, Kashima, Japan	50
Korea Fine Chemicals, Yeochon, Korea	60
Oriental Chemical, Kunsan, Korea	33
Tinguang Chemical, Lanzhou, China	40
Taiyuan Chemical, Taiyuan, China	20
Wusong Chemical, Shanghai, China	10
South America	
Dow-Pronor, Camacari, Brazil	60
Petrochemical Rio Tercero, Cordoba, Argentina	24

On a global basis, Europe has the largest capacity for TDI with some 768 Ktonnes/yr. of capacity in its eight plants. Bayer dominates European production with 497 Ktonnes/yr. of capacity, thanks in part to its large facility in Spain. Lyondell acquired access to Rhone-Poulenc's capacity through a joint venture agreement and then last year Bayer bought the company's urethane business in Europe and North America.

Asia is dominated by the Japanese TDI plant with 176 Ktonnes/yr. of capacity out of a regional capacity of 339 Ktonnes/yr. The plants in China and Korea are the size of the Japanese facilities with none larger than 60 Ktonnes/yr.

South America boasts two TDI plants for a total of 84 Ktonnes/yr. of capacity.

3.2.2 Outlook for TDI

Growth in TDI demand over the next few years has been projected in the 5-6% range annually.

Region	Demand Growth (% annually)	Capacity Additions (Ktonnes/yr.)
North America	5.2	306
Europe	2.8	90
Asia	6.9	260
South America	3.0-4.0	-
TOTAL	5.1	656

In North America, Dow Chemical has announced adding 100 Ktonnes/yr. of capacity at Freeport, TX with plans for an additional plant of the same size. Bayer also is planning to bring on 100 Ktonnes/yr. of capacity at Baytown, TX.

Asia has been a net buyer of TDI and capacity is planned for that region. Lyondell acquired the Arco TDI business, along with plans for a facility in Indonesia. That plant has been put off until 2004 or until the economic and political situation in that country settles down. Bayer is going ahead with a \$1.0 plus billion polyurethane complex at Caojing, near Shanghai that will include both an MDI and TDI facilities. The complex is slated to be completed in the 2005-2006 time period.

A second thrust in China for urethane chemicals is an isocyanate complex being studied by BASF, Huntsman and several Chinese partners. The consortium is planning a complex in the Shanghai area with a price tag in the \$1 billion range. Once approvals are obtained, the complex will take three years to complete.

South America is unlikely to see expansion of its TDI capacity. Growth is modest and economic uncertainty is going to affect long term investments in the region for some time.

On a short-term basis TDI markets are slightly over-supplied. However, the outlook in the sector is for the supply to become tight early in 2002, even with the additional global capacity coming on stream.

Rising raw material costs and the inability to raise prices has been the major concern of the TDI sector, and at this point prices are below reinvestment levels.

3.2.3 Regional use of TDI

The regional demand for TDI in Western Canada lies in flexible foam for cushioning and furniture applications as well as carpet underlayment. There is a RIM operation (Reaction Injection Molding) in Manitoba that likely uses some TDI in its operations.

Province	2000	1999	1998	1997
British Columbia	0.56	0.4	0.6	0.2
Alberta	0.45	3.1	3.4	2.7
Manitoba	Small	Small	Small	Small
Rest of Canada	33.4	27.9	23.4	21.8
TOTAL	34.4	31.4	27.4	24.7

Overall, the use of TDI in Western Canada is small and imports have been variable to the region. Any plant located in Alberta would have to serve the Canadian and US markets with good potential for exporting to the Pacific Rim countries.

Company	Major Product Area
A-Z Sponge & Foam, Annacis Island, BC	Furniture, carpet underlay foam
Carpenter-Jackson, Calgary, AB	Furniture, carpet underlay foam
Chemcrest, Winnipeg, MB	Molded furniture
Vitafoam Products, Calgary, AB	Bedding, furniture foam

As the flexible urethane foam business has matured and environmental and OSHA regulations tightened in the manufacturing plants, the number of flexible foam operations across Canada has declined. There has been little new applications for TDI to take the place of flexible bedding, carpet and molded foams.

3.2.4 Technology Change in TDI Applications

From a technology point of view TDI is the more mature of the isocyanates. Since TDI's demand is driven almost wholly by the flexible urethane foam business, most of the recent innovation has been in the molded products aimed at obtaining good outer skins to the seating and other items. This market segment consumes 90% of the material.

The flexible foams using TDI compete with latex and some of the other polymer foams such as polyethylene, and rubber. This is particularly true in uses such as carpet underlayment where competition is fierce. Being a large market the carpet segment has pushed suppliers to innovate to the point of using recycled foam along with fresh chemicals, as well as chemicals that have been recycled by breaking apart the chemical bonds of the plastics such as PET bottle resins.

3.3 Methyl Di-isocyanate

Methyl di-isocyanate or MDI is the purer form of the chemicals with polymeric or PMDI as the volume product. In production, polymeric MDI is produced and pure MDI is distilled out of a plant's basic product flow (on very small-scale).

3.3.1 MDI Producers

The MDI plants in North America are owned by the global urethane chemicals players – Bayer, BASF and Dow. The Rubicon joint venture has seen the ICI portion switched over to Huntsman, which is also in the polyol business.

Table 3.3.1 -1. MDI Plants in North America	
Plant	Capacity (Ktonnes/yr.)
BASF, Geismar, LA	225
Bayer New Martinsville, WV	50
Bayer, Baytown, TX	198
Dow Chemical, La Port, TX	160
Huntsman/Rubicon, Geismar, LA	300
TOTAL CAPACITY	796

Generally, the MDI plants in North America are of a good world-competitive size. MDI is generally produced at urethane complexes where TDI, aniline and other intermediate chemicals are produced. Recent expansions of MDI capacity have been made by BASF and Rubicon at Geismar, LA.

The European MDI plants tend to be smaller and older than those in North America, in part, because of the development of urethane chemistry on that continent. European capacity runs at 841 Ktonnes/yr. with Bayer dominating capacity. The Huntsman, Rozenburg plant in Holland is the largest in Europe and around the world at this time.

Table 3.3.1-1. MDI Plants on a Global Basis	
Plant	Capacity (Ktonnes/yr.)
Europe	
Bayer, Krefeld, Germany	60
Dow, Stade, Germany	80
Huntsman/ICI, Rozenburg, Netherlands	290
BASF, Antwerp, Belgium	140
Bayer/Shell, Antwerp, Belgium	36
EniChem, Brindisi, Italy	60
Bayer, Tarragona, Spain	60
Dow, Estarreja, Portugal	60
Ukraine	30
Hungary	25
Asia	
Nippon Polyurethan, Shin Nanyo, Japan	100
Sumitomo-Bayer, Niihama, Japan	67
Mitsui Chemicals, Omuta, Japan	55
Dow-Mitsubishi, Yokkaichi, Japan	36
Takeda-BASF, Kashima, Japan	30
BASF, Yeochon, Korea	80
Dow, Yeochon, Korea	25
Kumho-Mitsui, Yeochon, Korea	20
China,	10
South America	
Bayer, Nova Ignacu, Brazil	20
Brasileira de Poliuretanos, Camacari, Brazil	10

Asia is dominated by Japanese MDI capacity, while Korea boasts three plants among the 423 Ktonnes/yr. of capacity in the region. In South America Brazil has two small MDI facilities with some 30 Ktonnes/yr. of total capacity.

3.3.2 Outlook for MDI

Growth in PMDI has been running at 5-7% annually in recent years pushing the suppliers to debottleneck their facilities as well as consider expansion of capacity. Rigid foams for insulation; refrigeration and the other applications have been leading the demand push. Slowing construction markets could soften PMDI demand in the short term, but the long-term outlook is for continued growth across North America.

On a regional basis, the use of PMDI as a binder for the core of oriented strand board (OSB) caused demand to jump dramatically in Western Canada. Some of the producers of OSB have been refining their use of isocyanate and that along with some market shifts has slowed demand. The OSB sector in Canada increased its capacity by some 35-40% over the past half-decade, but most of the operations use phenolic binders throughout their operations. Persuading other OSB producers to utilize isocyanate for their core production could add 20-40 Ktonnes of PMDI to the Canadian market.

Overall, much of the MDI demand growth has come in China and this usage has pushed BASF and Bayer to plan major investments in that country. However, the economic conditions in Asia may cause a slowing of urethane growth, which has been as high as 10% annually in recent years to the more modest figures of 5%. This will reduce some of the supply pressure the urethane users have been facing. However, both the North American and Asian markets are expected to have solid growth in the coming years, and new capacity will be required to meet that demand.

MDI capacity in North America is set to rise as producers both replace older plants with ones with new technology and look to add overall capacity. Dow is replacing its Freeport, TX MDI facility with a 240 Ktonnes/yr. facility and has announced plans for an identical plant in 2006 or so. The LaPorte, TX MDI plant that Dow has will be closed when the new Freeport facility comes on stream.

3.3.3 Regional Use of MDI

The regional demand of MDI or PMDI has been growing because of the construction products sector – its use in OSB and strawboard. The bulk of demand in Alberta and Manitoba is connected to this market segment, while BC has a strong, but lower demand from the OSB sector.

Province	2000	1999	1998	1997*
Alberta	10.5	15.0	3.5	0.2
British Columbia	2.5	3.6	0.9	0.6
Manitoba	5.0	7.2	0.3	0.1
Saskatchewan	0.3	0.9	-	small
Regional	18.3	26.7	4.7	1.0
Ontario	33.8	38.7	32.2	6.3
Quebec	1.0	2.5	2.9	0.2
New Brunswick	0.1	0.2	-	-
% Western	34%	39%	12%	13%
TOTAL	53.3	68.1	39.9	7.4
* Statistics Canada changed the classifications in 1997.				

Imports into Manitoba jumped in 1999 when the Isoboard plant at Eli, MB came into production. The subsequent years have not been as strong for this facility and importation slowed. However, the take-over by Dow Chemical may revive the plant's operations and the requirement for PMDI.

The consumption of pure MDI is in the tonne range rather than kilotonne. In recent years, the use has dropped likely because specialty PMDI grades can handle the technical performance. In addition, manufacturing rationalization in Ontario may have had an effect as well.

Province	2000	1999	1998	1997
Alberta	24.7	143.7	106.7	26.3
British Columbia	-	41.3	111.5	97.8
Manitoba	-	56.7	36.3	308.3
Saskatchewan	-	3.7	1.2	0.2
Ontario	202.2	1,307.8	1,450.1	1,187.9
Quebec	31.6	260.3	93.6	61.7
Nova Scotia	-	133.6	-	-
TOTAL	258.5	1,947.2	1,799.4	1,682.2

Polymeric MDI's regional growth has been its use in oriented stand board (OSB), and strawboard. Isocyanate is used to bind the center core of the product, and the phenolic binder still is used on the top and bottom layers of the product. The isocyanate provides both good strength and cures up readily. While the penetration among the two dozen or more OSB plants in Western Canada is low, the use by just a few has caused the use of MDI to jump in recent years.

Ainsworth Lumber	100 Mile House, B.C.
Ainsworth Lumber	Grande Prairie, AB
Louisiana Pacific	Dawson Creek, BC
Louisiana-Pacific	Minitonas, MB
Weyerhaeuser Canada	Drayton Valley, AB
Weyerhaeuser Canada	Slave Lake, AB
Eastern plants	
MacMillan Bloedel	Wawa, ON
Malette Inc	Timmins, ON

A similar application has been the production of building board from straw at Eli, Man, This plant went into production in the late '90's and despite a fire made inroads into the market before running into problems. Dow Chemical has taken over the facility and as a major PMDI supplier will be able to use the facility to promote the technology as well as their product.

The bulk of the rest of the regional MDI market lies in the insulation and refrigeration sectors. In those areas, the urethane processors with larger operations bring in MDI directly from the US. The smaller firms buy systems – an A and B package of isocyanate and polyol. Much of those chemicals are blended by systems houses in Eastern Canada and shipped west. That volume shows up in the Ontario imports of MDI as well as polyurethane chemicals classification, which includes a variety of pre-formulated urethane chemicals.

Table 3.3.3-4. Some of the Rigid Urethane Users in Western Canada

Company	Location	Major Products
Coldstream Products Can	Winnipeg, MB	Refrigeration
Faroex	Gimli, MB	RIM Processing
Fibertech Ltd.	Vernon, BC	Rigid Foam
Fleck Bros.	Vancouver, BC	Insulation
R-Plus Industries	Calgary, AB	Insulation
Structural Glass	Winnipeg, MB	RIM processing
Chemcrest Corp	Winnipeg, MB	Furniture

A considerable portion of the rigid insulation and other rigid foam applications is supplied by 'systems houses'. These firms mix up a polyol blend of polyol, catalyst, blowing agent, etc. to produce a product that when mixed with the isocyanate produces the desired urethane foam. The systems houses usually sell drums of mixed polyol and MDI as a package, and most of the large systems houses are located in Ontario. As a result a portion of the Western demand for rigid urethane foam is supplied on a chemicals basis from Ontario and shows up as Ontario imports of MDI, polyols or even urethane chemical mixtures.

3.3.4 Technology Change in MDI Applications

Overall the rigid urethane sector, particularly the insulation and refrigeration areas, are fairly mature. Urethane foams are well proven. Even in the molded furniture area the self-skinning technology is well developed.

Isocyanate foams have been a slowly growing technology in the insulation field, where these MDI-rich systems offer better fire resistance than a conventional urethane.

3.4 Aniline and Nitrobenzene

The major raw materials for making MDI are nitrobenzene and its derivative aniline. Nitrobenzene production is generally tied completely to aniline production and there is little merchant demand. Aniline's major use is MDI, but some 20% of demand is in other chemical uses.

Rubber processing chemicals account for over 10% of aniline demand. Herbicides and dyes/pigments both use about 3% of aniline consumption. The specialty fiber business involves the production of spandex and other specialty yarns. Explosives, epoxy curing agents and pharmaceuticals round out aniline demand.

Segment	Percent Use
MDI (p,p-methylene diphenyl di-isocyanate)	80.0
Rubber chemicals	11.0
Herbicides	3.0
Dyes & pigments	3.0
Specialty fibers	2.0
Miscellaneous	1.0
TOTAL	100.0

3.4.1 Aniline Producers

The core of aniline production is based on a nitrobenzene hydrogenation process and is carried out by the urethane chemical companies. There are two firms that produce aniline on a co-product basis. Aristech has its Halcon process that involves the ammonolysis of phenol. It produces aniline and diphenylamine. Bayer's aniline production comes from a process that reduces iron filings to iron pigments using nitrobenzene and generates aniline as a by-product.

Table 3.4.1-1. Producers of Aniline in North America	
Producers	Capacity (Ktonnes/yr.)
Aristech, Haverhill, OH	68
BASF, Geismar, LA	105
Bayer, Geismar, LA	18
Du Pont, Beaumont, TX	127
First Chemical, Baytown, TX	114
First Chemical, Pascagoula, MS	110
Rubicon, Geismar, LA	227
TOTAL	769

Over 50% of aniline capacity now is handled by merchant producers or semi-merchant ones. First Chemicals is a large supplier, despite being a joint venture with Bayer. DuPont and Aristech are the other merchant suppliers to the chemicals sector.

3.4.2 Nitrobenzene Producers

Generally the nitrobenzene capacities of the various producers is balanced with the associated aniline plant, which in turn for some urethane complexes is sized to the MDI capacity on site.

Table 3.4.2-1. Producers of Nitrobenzene in North America	
Producers	Capacity (Ktonnes/yr.)
BASF, Geismar, LA	140
Du Pont, Beaumont, TX	173
First Chemical, Baytown, TX	155
First Chemical, Pascagoula, MS	227
Rubicon, Geismar, LA	318
TOTAL	1,013

Expansion of nitrobenzene capacity is underway in the sector. BASF is planning to add 73 ktonnes/yr. at Geismar, LA. First Chemicals plans to double its Baytown facilities, which are a joint venture with Bayer. This should be completed by the end of 2001. Rubicon has announced expansion of its MDI capacity by 50% and that will also include expanding aniline and nitrobenzene capabilities by a similar amount.

3.4.3 Outlook for Aniline and Nitrobenzene Regionally

Canada has no importation of nitrobenzene, so it has not market potential outside of any potential MDI investment. Aniline is pretty much in the same situation, although there are a few tonnes of material brought in each year.

Year	West Volume	Canadian Volume
2000	-	4,182
1999	-	36.6
1998	4.9	23.0
1997	0.8	16.6

Note: figures are in tonnes

The North American market has been running in the order of 750 Ktonnes/yr. with imports supplying 5-6 Ktonnes and the balance domestically supplied.

Despite a lack of regional demand a cost-competitive aniline plant coupled with an MDI, facility might be considered as a Pacific Rim supplier. Global demand for MDI is running at 8% annually with much of the use coming in Asian markets. While isocyanate plants are being built in that region, it continues to be supplied by exports from the US, offering potential opportunity to an Alberta producer.

3.5 Urethane Polyols

The global urethane polyols business runs to US\$ 1.3 billion in 2000 and amounts to some 1,397 Ktonnes of products. The chemistry of urethanes is sufficiently complex that a host of products are used as the 'B'-side of the urethane reaction. Some of the polyols are consumed in volumes as low as 20 Ktonnes/yr.

The dominant polyols are sorbitol-based products, and they account for over 70% of the polyol market globally or just over 1,000 Ktonnes of product. These polyether products dominate the flexible urethanes area and are used in rigid polyurethanes as well.

However, some of the other major polyol types include those made with sucrose, glycerine and mannitol.

Major Types of Urethane Polyols

- Sorbitol polyether polyols
- Polyester polyols
- Other Polyether polyols
- Other specialty polyols

The basic reaction for making ester polyols involves the reaction of propylene oxide or ethylene oxide with an 'alcohol'. Sorbitol, sucrose, glycerol, glucose, cellulose and pentaerythritol are alcohol examples, and a catalyst such as sodium hydroxide, potassium hydroxide, boric acid, trimethylamine, sodium methoxide, trimethylpiperazine, or sodium methoxide is used. The reaction often is carried out in a solution of water, xylene, DMSO or else without a carrier.

3.5.1 Polyol Producers

Producers of urethane polyols split into two groups – the major urethane chemicals producers, and the specialty chemical producers. All of the major urethane chemical firms – Bayer, BASF, Dow and Huntsman – produce the isocyanates and polyols along with some of the urethane additives and modifiers.

The specialty polyol chemical firms include companies such as Arch Chemicals, SPI Polyols, Ruco, Inolex, SW Urethane and the like. A major merchant supplier of sorbitol for the urethane polyols business is SPI Polyols as well as a polyol producer. With the pot chemistry involved in polyol production, firms in the surfactant business – Witco and Stepan – also are polyol suppliers based on product technology and good fit with their manufacturing plants' capabilities.

Major Polyol Producers

- Arch Chemicals Inc., Brandenburg, KY
- BASF Corporation, Parsippany, NJ
- Bayer Corp., Polyurethanes Division
- Dow Chemical, Freeport, TX
- Huntsman Corporation, Mississauga, ON; Conroe, TX
- Harvin Reaction Technology Inc., Greensboro, NC
- Inolex Chemical Co., Philadelphia, PA
- Oxid L.P., Houston, TX
- Ruco Polymers, A Sybron Chemicals Co., Hicksville, NY
- SPI Polyols, Mapleton, IL
- SWD Urethane Co., Mesa, AZ

- Stepan Chemical, Northfield, IL
- Witco, A Crompton Business, New York, NY

3.5.2 Outlook for Urethane Polyols

Overall growth in urethane polyols runs in the 3 to 4% range at this point, slightly lower than that for MDI and about equal to TDI growth rates. In North America polyol consumption is fairly mature with isocyanate getting a lift from non-polyol use applications such as OSB and other construction products.

Generally, the polyol business is a fairly regional one with little international trade. It is likely to remain that way since the urethane processors and the systems houses require a variety of polyol products to serve their customers' needs. As a result the polyol producer is a true specialty chemical firm, tailoring product to particular niche applications.

3.5.3 Regional Use of Urethane Polyols

There are no import figures on polyols, per se, since they come into Canada under several classifications that mix them in with a host of other chemicals as well.

A rough estimate can be made of the polyol consumption based on the use of TDI and MDI in the region and subtracting off the OSB/construction use of MDI. However, complete systems traditionally have been shipped out West by the Ontario urethane systems houses, and that volume may not be reflected in the estimate.

Product	Estimated Use* (Ktonnes/yr.)
Sorbitol polyethers	4.1
Other polyols	1.4
TOTAL ESTIMATED	5.5
* Based on 2000 import figures	

3.5.4 Technology Change in Polyol Applications

Over the past few years, polyester polyols have taken over in some rigid urethane systems, due to better stability in more severe environments and weather conditions. As mentioned earlier, mannitol has been moving into the urethane polyol area as a base for making polyester type products.

For the low end of the urethanes business, polyols from recycled PE products have been used. A couple of firms crack PET into glycol and other components and obtain a polyol that is suitable for urethane reactions. The polyester polyol from these operations have been finding some application.

3.6 Propylene Oxide

Propylene oxide use in North American is at the 1,450-kilotonnes/year level. The polyether polyols demand dominates its applications, but at modest growth. The environmental regulation on coatings and adhesives has been driving the other major application areas.

The concerns in the solvents market about VOC emissions have given a boost to the P-glycol ethers and propylene glycol. Both of these application areas have been growing at 4-5% annually, but from a small propylene oxide use base. Dow invested in a major glycol facility in Texas, while Shell has moved into the glycol ethers in support of its solvents business.

Segment	Percent Use
Urethane polyether polyols	60.0
Propylene glycols	25.0
P-series glycol ethers	4.0
Miscellaneous	11.0
TOTAL	100.0

The miscellaneous uses of propylene oxide include polyalkylene glycols, allyl alcohol and isopropanolamines. These specialty chemicals account for some 11% of propylene oxide demand.

3.6.1 Propylene Oxide Producers

Lyondell has the largest propylene oxide capacity in North America, but only exceeds Dow's capacity by 175 Ktonnes/yr. Huntsman is the third producer in the sector with a plant scaled to its urethane business.

Table 3.6.1-1. Major Propylene Oxide Producers in North America	
Producer	Capacity
Dow, Freeport, Tex.	590
Dow, Plaquemine, La.	285
Huntsman, Port Neches, Tex.*	180
Lyondell, Bayport, Tex.*	550
Lyondell, Channelview, Tex.*	500
TOTAL	2,105
* co-product capacity	

The Lyondell plants are using a co-product process with the Channelview facility boasting a POSM – propylene oxide/styrene monomer – process for making styrene. The Bayport plant produces tertiary-butyl alcohol as its coproduct. Huntsman's plant uses a similar process to Lyondell Bayport except it generated MTBE instead of TBA. The economics of co-product routes to propylene oxide has been causing a shift in the competitive position of processes. While MTBE may be under the gun in California, TBA and styrene have fairly strong markets, hence, the competitive position of reacting propylene with benzene or isobutene.

3.6.2 Outlook for Propylene Oxide

Growth in propylene oxide has been reviving as urethanes remain solid and propylene ethers and glycols grow as solvent replacements in the coatings, adhesives and inks areas. Dow Chemicals has plans for a POSM facility in Freeport, TX, but the 200 Ktonne facility has been put off until 2004 due to market conditions.

3.6.3 Regional Use of Propylene Oxide

The regional demand for propylene oxide is minimal – in the tonne range - where the Canadian use runs in the 50+Ktonne level. Therefore, the major support for a propylene oxide investment lies in the domestic Canadian market in Eastern Canada. Their imports have been running in the \$55-85 million range in the past few years.

Year	West Volume (tonnes)	Canadian Volume (tonnes*)	Canadian Value (\$million)
2000	0.3	44,160	\$ 54.6
1999	0.4	51,500	\$ 73.9
1998	0.4	58,500	\$ 88.5
1997	139.1	57,100	\$ 83.9
Note: figures are in tonnes. * rounded			

Changes in the surfactant business have seen the volume and value of propylene oxide imports drops slightly, the rationalization of the customer base is likely complete. Expectations are that demand will stabilize and propylene oxide imports will slowly rise in the coming years.

3.6.4 Technology Change in Propylene Oxide Applications

The reduction of VOC emissions in the paint, inks and adhesives area has been a boost to propylene oxide demand, as propylene glycols and propylene esters have been used to reduce the use of more volatile solvents. The P-series glycol ethers and di and tripropylene glycols have been growing 12% more than the overall propylene oxide demand in North America.

The heavier solvents such as the Pseries ethers are offered by the major solvent producers with companies such as Shell Chemicals moving into their production in recent years.

Company	Location	Solvent Product Line
Arco Chemical Co.	Newton Square, PA	P-series glycol ethers N-methyl-pyrrolidone (NMP) methyl ter-butyl ether
Dow Industrial	Midland, MI	P-series glycol ethers chlorinated solvents
Eastman Chemical	Kingsport, TN	P-series glycol ethers, butyl acetate, butanol
Occidental Chemical Corp.	Dallas, TX	P-series glycol ethers Benzotrifluorides, Monochlorotoluene and perchloroethylene mixes
Shell Chemicals Co.	Houston, TX	P-series glycol ethers cycloparaffin solvents methyl propionate
Source: SRI Consultants and Sigurdson & Associates		

In areas such as polyols, competition between ethylene oxide and propylene oxide may intensify as producers utilize new and different alcohols for their products.

3.7 Sorbitol

Commercial production is by high-pressure catalytic hydrogenation of glucose sugar derived from cornstarch. Sorbitol can be produced as a coproduct with mannitol if invert sugar (50% glucose, 50% fructose) is used as raw material.

Market Segment	Percent of Demand
Toothpaste, toiletries and cosmetics	35
Confections and food	30
Ascorbic acid	15
Industrial surfactants	10
Pharmaceuticals	7
Misc., including polyethers for polyurethanes	3
TOTAL	100

In a North American Sorbitol market of 270 Ktonne, the use of the chemical to produce polyol esters for urethane business accounts for under 8 Ktonnes/yr. Interestingly mannitol is being used as a base for making urethane polyols as well as sorbitol.

3.7.1 Sorbitol Producers

There are five Sorbitol producers in the US, each with fairly developed niches in the overall market. ADM has a large sweetener and specialty chemicals business focused on fermentation chemistry. Hoffmann-La Roche uses its sorbitol capacity captively in the production of ascorbic acid, which fits with its vitamin business.

Table 3.7.1-1. Major Sorbitol Producers in North America	
Producer	Capacity (Ktonnes/yr.)
ADM, Decatur, Ill.	68
Hoffmann-La Roche, Belvidere, N.J.	27
Lonza, Mapleton, Ill.	50
Roquette America, Gurnee, Ill.	68
SPI Polyols, New Castle, Del.	56
TOTAL	269

SPI Polyols Inc. bought the US-based polyols business of ICI Americas in 1994, and then purchased Ethichem Corporation's sorbitol business in June 1998. Ethichem's 30-million-pound plant at Easton, Pa. has been dismantled and some of the equipment moved to SPI's New Castle site. ADM bought Pfizer Inc.'s sorbitol business in 1994 to add to its fermentation businesses.

3.7.2 Outlook for Sorbitol

The Sorbitol demand in North America is expected to grow at 3% annually and perhaps could rise to 4% level, if the economic outlook strengthens.

Toothpaste and food applications have been the bulwark of the Sorbitol business and competition from mixtures of other polyol with Sorbitol has softened growth. Sugarless gum has been using crystalline Sorbitol and experienced growth in the chewing gum market.

Industrially other polyols such as glycerin, propylene glycol, mannitol and xylitol have been offering competition. Ascorbic acid use of Sorbitol has been facing offshore competition from imports from countries such as China and India.

3.7.3 Regional Use of Sorbitol

Overall, in the context of urethane polyols Sorbitol and mannitol use in Canada has been minimal. Sorbitol use has been as high as \$88,000 recently, but no imports in 2000. Mannitol imports have been as high as \$14,000. Pentaerythritol has a more solid position, as a chemical with imports amounting to \$17 million, however as a urethane chemical its use is modest.

Table 3.7.3-1. Imports of Sorbitol & Other Polyalcohols					
<i>(Canadian Dollars)</i>					
Product	1996	1997	1998	1999	2000
Pentaerythritol	8,915,613	16,021,739	19,313,090	17,358,831	17,136,806
Mannitol	--	11,504	7,735	5,747	14,147
Sorbitol	--	239,070	20,432	88,433	--
TOTAL	8,915,613	16,272,313	19,341,257	17,453,011	17,150,953

Therefore, as with propylene oxide the regional demand in Western Canada is almost nil. Any urethane polyol investment in Alberta would involve selling to the US likely with the importation of Sorbitol or other alcohols.

4.0 ISOCYANATES

4.1 Introduction

While a variety of isocyanates are used, only MDI and TDI are of major importance. While others can be considered as “add-on” products at an isocyanates facility, they are generally neglected herein. The TDI facility is now seen as being built only in concert with an MDI facility as only very marginal economics are foreseen for a standalone TDI plant.

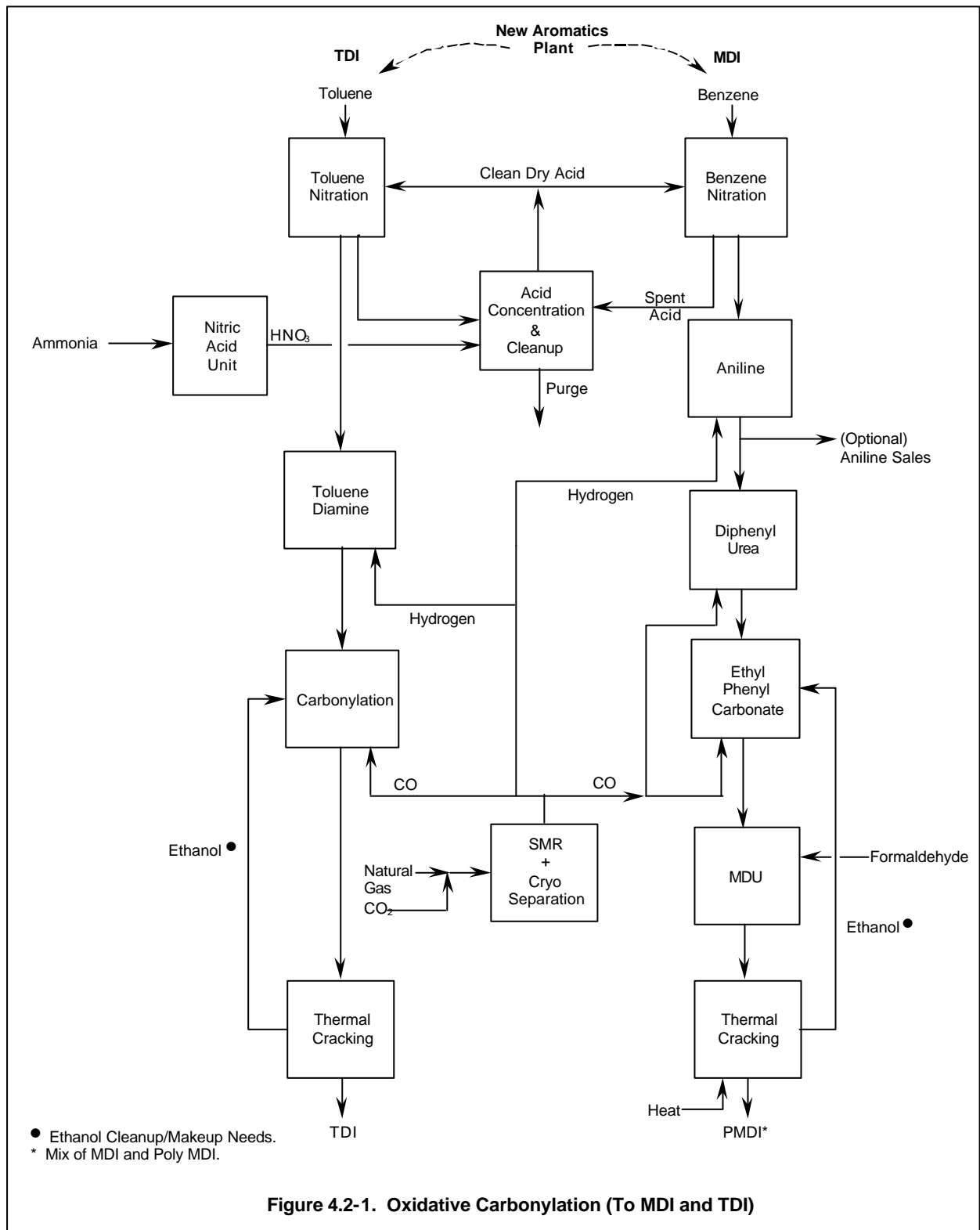
This study considered MDI, methylene diphenyl isocyanate, and TDI, toluene di-isocyanate, as these are currently the principal isocyanates. Smaller-scale isocyanates might be considered in a commercial complex, but their production would be batch or during short campaigns. This study did not consider such opportunities, and their feedstocks.

4.2 Material Balances and Process Modules

Table 4.2-1 provides preliminary material balances for a nominal 100-KTA of MDI and 50-KTA of TDI matching the flow scheme of Figure 4.2-1. The balances are preliminary and useful largely to identify feedstock needs and related sources. The 100-KTA scale for MDI was selected as the smallest likely to be competitive in global markets. As noted above, Dow plans a 240-KTA facility on the USGC and, further studies will hopefully raise the appropriate scale of an Alberta plant.

Virtually all current isocyanate production uses a phosgene (COCl_2) intermediate and CO for the final product. As the footnote to the table indicates this study concluded that a non-phosgene route would be most likely for new Alberta facilities and oxidative carbonylation was selected for illustration of such an alternate for the final steps in MDI and TDI production. However, a phosgene route integrated with enhanced ethylene dichloride production is briefly discussed.

Table 4.2-1. Isocyanate Material Balance				
Bases: Product Rate	MDI	TDI	Total KTA	Notes: MDI = PMDI
	100 KTA	50 KTA		
Final Process Steps Assumed:	Oxidative Carbonylation ⁽¹⁾			Considered commercially attractive - No Phosgene or Chlorine - Participant brings own process - Schemes per Gunardson pages 250 and 251 ⁽³⁾
Flow Schemes	See next page			
External Material Balances			Source (Transport)	
Benzene	66	--	(66)	Pipeline
Toluene	--	21	(21)	Pipeline
NH ₃	16	9	(25)	Tank Car for HNO ₃
Formaldehyde	15	--	(15)	Truck
Oxygen	16	7	(23)	Pipeline
CO ₂	15	7	(22)	Pipeline to balance H ₂ & CO production.
Natural Gas	to be defined			Pipeline Fuel and CO and H ₂
H ₂ SO ₄	to be defined			Truck for HNO ₃ drying/activation
Nitrogen	to be defined			Pipeline Blanketing, etc.
Electricity	to be defined			Consider Cogen ⁽²⁾
Byproducts	to be defined			Sell/Dispose of
Internal Material Balances				
HNO ₃ (100%)	54	28	(82)	Make on Site
CO	26	13	(39)	Make on Site
H ₂	3	3	(6)	Make on Site
Steam	to be defined			Make (Consider Cogen) ⁽²⁾
⁽¹⁾ No Phosgene Route - GE has ruled out use of phosgene in all new polycarbonate facilities and except perhaps for China - e.g., Bayer at Shanghai - no phosgene use is expected in the future at new MDI/TDI facilities. But a (remote?) prospect in Alberta integrating phosgene-based isocyanates is noted later. ⁽²⁾ Integrate steam with CO/H ₂ . ⁽³⁾ Gunardson, H. "Industrial Gases in Petrochemical Processing" 1999.				



4.3 Feedstock Availability

Benzene

- The study sees added aromatics supply to serve major new styrene and possibly other derivative markets. (Note that a major new aromatics complex would also have toluene and xylenes available.) An MDI facility will only need 15 to 20% of the benzene needs of a major new styrene plant.
- Currently, however, the 66-KTA needed for the 100-KTA MDI facility are not readily available. The existing benzene producer is running flat out and at least one now exported ethylene byproduct stream containing benzene is committed to US markets for several years.
- An earlier 2001 study indicated major new benzene potential at an Edmonton refinery with major capital, but synergies with current and planned operations. Other smaller prospects were also identified. Benzene availability for a major new derivative plant may be largely a matter of negotiation.

Toluene

- While there appears potential for new toluene production at two Alberta refineries, the unit cost would be high due to need for added reformat distillation and an extractive distillation system for a relatively small quantity. As TDI is the marginal isocyanate, unlikely to be economic on its own, this "potential" was not explored.
- A new major benzene source will almost certainly have toluene available, with all in excess to gasoline and conversion benzene (and perhaps xylenes).

Ammonia

- Discussions with Agrium indicate delivery likely by rail unless next to Redwater site.

Formaldehyde

- Formaldehyde has been assumed available from one of the existing Edmonton area producers.

Oxygen

- Oxygen will be available by pipeline in the AIH, Edmonton and Joffre areas.

CO₂ (To Balance CO and Hydrogen Production)

- CO₂ is available in the AIH and with purification could be in the Edmonton area.

Natural Gas

- Natural gas for CO/H₂ production and as fuel is readily available.

4.4 Process Review

4.4.1 General

The following notes briefly review the key processes shown in Figure 4.2-1. Process details have not been developed in most instances, but the processes except for those from aniline and diamine to MDI and TDI are generally available from more than one technology licensor. The oxidative carbonylation processes will be operator provided both to match his experience and his environmental controls. The operator would if considered provide phosgene routes, with possible exception for phosgene production, where several licenses are available.

Due to the scale of the various units, it appears that shop built modules would predominate, building on Alberta's world leading capabilities and expediting the overall project.

Generally, the various process steps are not unlike those of several of the smaller units in the Celanese Edmonton complex. They are smaller-scale, more complex and technical than many of the other existing Alberta petrochemical processes.

4.4.2 Nitration and Related Acid Systems

The benzene and toluene nitration systems would use well-proven technologies to Kvaerner Chemetics (Vancouver) or others. A mixed nitric sulphuric acid is used as the latter activates the nitric acid. The acid solution becomes weaker in the process and the acid concentration unit removes water (via sulphuric acid concentration), as well as dissolved organics.

Both nitration and acid reconcentration processes are well known and despite very corrosive acid, high reliability is achieved with good safety.

4.4.3 Nitric Acid

This is a small-scale nitric acid unit, burning ammonia with air and then scrubbing the N₂O to produce HNO₃ at about 73% concentration. (Merchant sales should be considered to increase the size.) Very well proven technologies are available from Kvaerner Chemetics and several other companies. These

are energy-efficient units, with an excess of heat and in some designs, electricity available. NO_x and N₂O control are very important.

There are nitric acid plants today at Agrium Redwater and Orica Carseland – the former has none available for sale and the latter was considered too distant for, say a Fort Saskatchewan plant site.

4.4.4 Aniline

Again, this is a well-proven process, available publicly. The nitrobenzene is reduced to aniline plus water and the aniline redistilled to insure purity.

4.4.5 Toluene Diamine

This too is a well-proven, relatively simple process.

4.4.6 MDI Diphenyl Urea/Ethyl Phenyl Carbamate/MDN/and Cracking

These steps will be based on the plant operators' proprietary know-how. Here an oxidative route has been chosen in lieu of a reductive one. The "old" standard involved use of phosgene at milder conditions than required here. As noted above, a non-phosgene route is considered "almost" essential in a new North American plant at this scale. (Phosgene routes are discussed later.)

Gunardson's "Industrial Gases in Petrochemical Processing" provides review of both oxidative and reductive routes and his descriptions have been assumed for this study.

Aniline Oxidation to Diphenyl Urea

- Noble metal catalyst with iodine to incorporate CO and oxygen into the urea.

Diphenyl Ether to Ethyl Phenyl Carbonate (EPC)

- Oxidative carbonylation with more CO and oxygen added in presence of ethanol, with a palladium catalyst at 160°C and 80 atmospheres.

EPC Condensation with Formaldehyde to MDU

- This is done with a strong acid catalyst.

Cracking of MDU

- At roughly 250°C and 30 atmospheres, the MDU is cracked to MDI and ethanol (for recycle).

Note that the final product is a mix of MDI and polymers of MDI – a liquid, whereas MDI itself is a solid at room temperature. (Pure MDI produced via distillation has a limited market, but might be considered in the future.)

4.4.7 CO and Hydrogen

Low-pressure steam methane of natural gas augmented with CO₂ is proposed. The pressure is kept low to maximize CO yield from the steam methane reformer catalyst filled tubes. Unreacted and byproduct CO₂ would be scrubbed from the SMR effluent for recycle and then cryogenic separation used to produce relatively pure CO and hydrogen for use in various process steps. This is but a variation on most Alberta SMR to hydrogen units and is in common use elsewhere.

4.4.8 TDA Carbonylation and Cracking

The carbonylation route to TDI has fewer steps than to MDI, with the MDU type intermediate step avoided.

Operating conditions appear likely to be similar to those of the EPC and thermal cracking steps in MDI production.

4.5 Environmental Considerations

Traditionally MDI and TDI plants have used phosgene to activate and add CO. Phosgene however, is a serious environmental and public relations concern. The one Canadian TDI plant that of Allied Chemicals killed several cows early in its mid 1960's to 1980's life time, with phosgene venting when an ammonia injection system did not kick in properly. There was always the risk of worker and neighbouring community health risks.

This study concluded it would be very difficult, expensive and time consuming to obtain permits for and to use phosgene in a new Alberta isocyanate operation. This was, in part, based on reference to DuPont by an advisor. However, phosgene use in new isocyanate production in the Far East is expected to continue despite such issues. A phosgene route is briefly discussed in Section 4.6. This study selected an oxidative carbonylation route, but recognizes prospective operations will bring their own proprietary processes.

As Table 4.5-1 illustrates many of the chemicals in the MDI/TDI complex are more or less toxic. Facility designs must be based on proven technologies and provide for excellent control of all manner of releases in operations. Only an experienced operator is recommended, one with much current safe, completely environmentally friendly operations.

ILLUSTRATION ONLY

Table 4.5-1. MDI/TDI Production Chemical						
Product	Chemical	Allowance Concentration in Air (PPM)	Carcinogen	Toxicity	Corrosive	Flammable
M	Benzene	1	✓	A/C		✓
T	Toluene					✓
MT	Nitric Acid				✓	
MT	(Sulphuric Acid)				✓	
MT	Hydrogen					✓
MT	CO					✓
MT	CO ₂					
M	Formaldehyde	1	✓	A/C		✓
MT	Ethanol					✓
MT	Ammonia			A/C	✓	✓
MT	Oxygen					
M	Nitrobenzene	1	?	A/C		✓
T	Dinitrotoluene	(1.5 mg/m ³)	P	A/C		✓
M	Aniline	2	P	A/C		✓
T	Toluene Diamine	(solid)	P	A/C		✓
M	Diphenyl Urea	INFORMATION NOT COLLECTED AT TIME OF WRITING - Assume equivalent to MDI Product -				
M	Ethylphenylcarbamate					
M	MDU					
M	TDU					
M	MDI	0.005	P	A/C*		✓
T	TDI	0.005	P	A/C†		✓

P – Possible carcinogen
 A – Acute toxicity potential
 C – Chronic toxicity potential
 * – Some persons may be susceptible (hyper-reactivity)
 † – Some persons are susceptible (1/1000 or so)

4.6 PHOSGENE ROUTES TO DI-ISOCYANATES

While phosgene routes have generally been precluded from this study, due to extreme toxicity and public relations issues, there is some possibility of a fit with vinyl chloride production.

The phosgene route first reacts:

$$\begin{array}{ccccccc} \text{CO} & + & \text{Cl}_2 & \longrightarrow & \text{COCl}_2 \\ \text{Carbon} & & \text{Chlorine} & & \text{Phosgene} \\ \text{monoxide} & & & & \end{array}$$

with the phosgene used directly in the vapour phase in all major cases. (A small amount is condensed and delivered to specialty chemical producers in special containers, but careful control is essential.) Packaged phosgene production units are available from Kvaerner Chemetics in Vancouver and other process licensors/packagegers.

For MDI's, aniline, formaldehyde and phosgene are reacted to produce dimeric – two phenyl rings – and trimeric – three or more phenyl rings – MDI's, plus hydrochloric acid (roughly 55% by weight of MDI product) and water in well proven process sequences. Toluene di-isocyanate (TDI) is produced from toluene diamine and phosgene, again with appreciable HCl (84% by weight of TDI).

In the US, the hydrochloric acid (HCl) byproduct faces major market challenges and the same is likely here. (Currently, merchant HCl is brought into Alberta from BC for oil field and other uses.)

Approximately 550,000 tonnes of HCl from US isocyanate production was recycled to ethylene dichloride (EDC) production in 2000, with an increase to 656,000 estimated for 2003. About 65% of Dow's 4.5 x 10⁶ tonnes a year of EDC will be produced from recovered HCl by 2005 compared to 40% in 1995. Dow is the world's largest chlorine producer and second only to Bayer in isocyanates.³

The same article notes that US merchant HCl markets are expected to drop to 100,000 tonnes by 2003, due to reduced availability of byproduct HCl (some of which is often precluded from certain markets due to trace impurities).

³ Extracts from "Using HCl Recycling to Feed Chlorine Derivative Production" page 50 – Chemical Week, December 5, 2001.

Recycling of HCl into EDC is in itself more expensive than direct chlorination, but the HCl cost is much below that of chlorine:

Chlorination:	Ethylene + Chlorine → EDC
Oxychlorination:	Ethylene + HCl + Oxygen → EDC + Water
EDC Cracking:	EDC → Vinyl Chloride + HCl

Dow exports appreciable EDC from Alberta at the same time producing VCM for local and other markets. This tends to indicate that oxychlorination capacity is smaller than if only VCM is produced – a bottleneck to use of isocyanate byproduct HCl, requiring added capital in the EDC operation.

Thus, while this study has generally discounted phosgene routes to MDI and/or TDI there remains a possible fit with existing and/or new EDC with or without VCM production in Alberta. A phosgene route to di-isocyanates in Alberta would appear to require integration with at least EDC production via a new or expanded oxychlorination step.

4.7 MDI/TDI Complex Costs and Operations

The overall isocyanates complex capital costs appear likely to be in the \$500 to 600 million range – very dependent upon the processes selected by the operator. The non-phosgene routes tend to push up the costs due to more exotic operating conditions, but overcome the many challenges of producing and handling phosgene in larger-scale.

Dropping the TDI portion would probably only reduce capital costs by \$100 to 120 million, as most auxiliary processes serve both MDI and TDI trains.

The overall complex would require 100 to 130 employees – perhaps 20 less if TDI dropped.

Electricity would be the main utility in addition to natural gas, due to high compression costs. Several of the process units are net heat producers, but unfortunately, sufficient data were not available to assess. Very careful design and operation will be essential for protection of workers and neighbours. This almost certainly means operation by a very experienced operator, at least of the carbonylation reactions, downstream of aniline and diamine. Full involvement of regional health, emergency measures and neighbours in preplanning, permitting and operations overview will be essential. Overall, the proposed complex, its operation and management should prove environmentally friendly.

The overall complex appears likely to have minor greenhouse gases per unit of production. NO_x control on nitric acid flue gases will be important, but today this standard practice. Aqueous waste treatment will require extensive analysis, but again, good design should preclude adverse releases.

While the complex would fit into a 10-hectare plot, a significant buffer zone would be recommended so that 20 to 25 hectares is suggested.

5.0 POLYOL PRODUCTION

5.1 Introduction

There are many polyols! While here we are interested only in polyols relative to polymer ethanes, any polyol producer will produce a suite of polyols, but a suite very specific to his target markets. As the polyol components are usually in excess of the (expensive) isocyanate their cost is very important to the end user. Polyols are “performance” chemicals in the sense that the end user is interested only in their performance and cost in his polyurethane product. Chemical composition is only of secondary interest, if at all. While large polyol suppliers have a set of standard polyols, good chemists in smaller specialty chemical producers can often formulate special polyols to fit niche markets, making use of what feeds are economically attractive to him.

Safety and health aspects are, of course, of concern, but generally, polyols are quite benign virtually all polyurethane safety and health issues involving the isocyanate. Many polyols are used in food products, for example.

The final user receives a blend of isocyanate, OH rich material, various other chemicals to modify the final properties and a catalyst to accelerate the polymerization in the end users moulds. There are two major ingredients in polyol production – propylene or in some cases ethylene oxide (and/or one or more of their glycol derivatives) and a molecule with 3 to 10 or more OH groups to react with the isocyanate. This section reviews oxides, multi OH materials and blending in that order.

5.2 Propylene and Ethylene Oxides

5.2.1 Ethylene Oxide and Glycols

Ethylene oxide is not of major importance in polyol production (other used to “cap” off propylene oxide derived polyols), but ethylene glycols are possibly of greater use. In this section, we have put ethylene oxide before propylene oxide, only due to its current production in Alberta and the inherent ability to increase its production, except perhaps at time of peak glycol netbacks.

Some merchant ethylene oxide is produced in Alberta, with sale to distant specialty chemical companies. However, due to hazards in shipping, added ethylene oxide production will only be for fence line users.

Crude ethylene oxide is an intermediate in the production of ethylene glycols at Fort Saskatchewan and Joffre. The Fort Saskatchewan facility has (limited) ethylene oxide purification facilities for merchant sales. Such purification facilities are not complex, but the safety concerns of purified ethylene oxide are very important in their design and operations.

Ethylene glycols are potential polyol ingredients and already available here.

Ethylene Oxide Uses

- ETHYLENE GLYCOLS
- NON IONIC SURFACTANTS
- ACRYLONITRATE
- POLYOLS
- MISC. ORGANIC COMPOUNDS
- FUMIGANT
- STERILANT
- FUNGICIDE

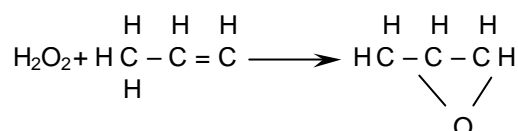
Ethylene Oxide Characteristics

- Boiling Point 10.7°C
- Melting Point -11°C (note)
- Mighty Flammable -4°C flash pt.
- Explosive
- Polymerizes Exothermically
- In Air 1-ppm (odour threshold 430)
- Carcinogenic
- Inhalation, Ingestion, Dermal Hazard
- Miscible in Water

5.2.2 Propylene Oxide and Glycols

a) Hydrogen Peroxide and Propylene

As this report was being written, BASF announced plans for a 220-KTA NAFTA or European propylene oxide facility based on a new BASF H₂O₂ plus propylene process (see side bar).



Degussa has also developed an H₂O₂ plus propylene to propylene oxide process and indicated interest in a Redwater/Gibbons area propylene oxide plant, using Degussa Gibbons H₂O₂ and Williams Energy's propylene (from the new fractionation system processing Suncor's crude propylene stream).

Both of these processes are proprietary, but investment in the \$80 to 200 million range feels likely with, say, 50 employees. Overall, reactions are likely to be exothermic and, hence, electricity may be the primary utility.

b) Epoxidation of Propylene

Direct oxidation of propylene is non-selective, with most propylene over-oxidized to CO₂. Peroxides are much more selective in "transferring" oxygen to propylene to produce propylene oxide. Currently, roughly 50% of propylene oxide is produced via peroxidation, largely as a coproduct, with styrene. Peroxidation is definitely the preferred route to propylene oxide today, but the above-noted hydroperoxide/propylene route appears likely to be attractive, at least at smaller-scale.

Both isobutane and ethylbenzene are used in conjunction with propylene to produce propylene oxide and tertiary butyl alcohol (TBA) and styrene respectively. In the isobutane route, the TBA could be converted to isobutylene for MTBE and/or polyisobutylene. North American MTBE usage appears likely to drop and polyisobutylenes are small-scale and do not appear to have major growth potential. The previous aromatic study noted – and as current indications appear to confirm – major new benzene supply in Alberta could well lead to major new styrene production.

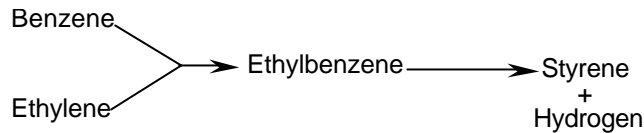
Propylene Oxide Uses

- POLYURETHANE POLYOLS
- PROPYLENE GLYCOL
- DIPROPYLENE GLYCOL
- GLYCOL ETHERS
- NON-POLYURETHANE POLYOLS
- ISOPROPANOL AMINES
- PROPOXYLATED SURFACTANTS
- PROPYLENE CARBONATE
- HYDROXY PROPYLATED CELLULOSE
- ALLYL ALCOHOL
- GLYCEROL via ALLYL ALCOHOL (glycerol is another polyol feed)

Propylene Oxide Characteristics

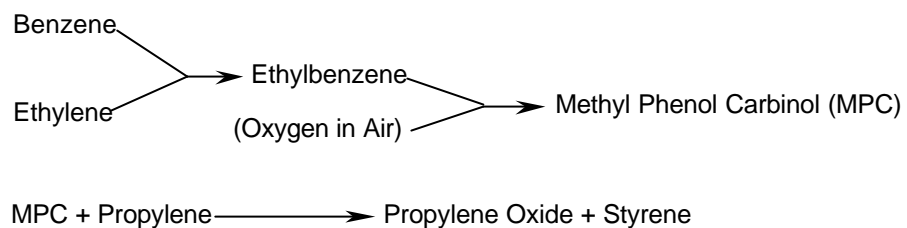
- Boiling Point 34.2°C
- Melting Point -112°C
- Extremely Flammable -35°C flash pt.
- Explosive/Polymerizes (with heat)
- Wide Flammability Limits -2.3-36% in air
- Polymerizes Exothermically
- In Air <20-ppm (odour threshold 44)
- Probable Human Carcinogen
- Inhalation & Dermal Hazards
- Very Soluble in Water

Styrene can be produced by the conventional route as used by Shell Chemicals at Scotford:



Where hydrogen purity is not great and there is some benzene recycle and polymers formed.

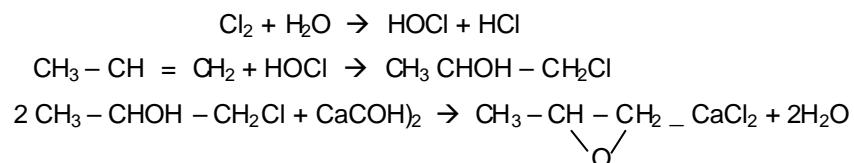
In the case of a POSM approach:



The POSM route requires favourable propylene oxide markets, preferred very nearby, thus, there is a good fit with local propylene oxide polyol production. A POSM plant will be large-scale at 500-KTA of styrene, roughly 270-KTA of propylene oxide will be produced. (Such a facility will need approximately 400-KTA of benzene, 140-KTA of ethylene and 210-KTA of propylene.)

c) Older Chlorohydrin Routes

The propylene chlorohydrin route to propylene oxide was the standard for many years:



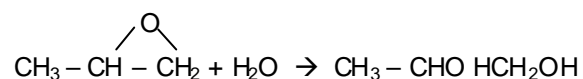
Approximately 0.1-kg of dichloride was formed per kilogram of propylene oxide. Disposal of the dilute brine waste was also a problem (even if sodium is substituted for calcium).

This route to propylene oxide feels very unlikely in Alberta.

d) Propylene Glycols

Aside from use in polyols, propylene glycols find many foods, cosmetic and industrial uses.

Propylene glycols are produced in a very similar manner to ethylene glycols.



With more water increased di, tri and polypropylene glycols production is achieved.

5.3 Polyol Production

Polyol production based on the feedstocks noted in Section 3.5 above is largely batch chemical based:

Reaction

- Reaction in solvent and/or water.
- Batch with some addition of reactants during the batch.
- 5 to 10,000 USG stainless steel reactors with jackets and mixers or external circulation / heating systems and mixers.
- Maximum pressure 10 atmospheres and temperatures to 200°C.

Solvent/Water Removal

- Distillation (pressures down to vacuum)

Packaging

- To drums or tote bins.

Auxiliary Processes

- For ingredient modification.

Utilities

- Steam, cooling water, vacuum, hot oil, air, etc.

Tankage

- Feedstocks, chemicals

Such facilities can cost \$15 to 80 million, depending on product range and to some extent capacities. Some of the larger suppliers have continuous and semi-continuous process sequences for large volume.

However, it is not envisaged that polyol production in Alberta would equal, say, propylene oxide production. However, at a propylene oxide plant, some preprocessing to propylene glycols and propylene oxide/propylene glycols based polyol bases is quite likely. These facilities are essentially those of many specialty chemical plants (and specialty polyols for non-urethane markets and non-polyols are very likely to be produced).

Sorbitol and perhaps mannitol production from Alberta sugars and starches can be considered, but the wide range of such polyol ingredients was considered beyond this study. Wheat starch is already being converted to glucose for ethanol production at Red Deer and potato starch is available in large quantities.

6.0 SUMMARY

This study concentrated on the large volume ingredients going into polyurethane manufacture – the two principal isocyanates, polyols (generically) and their principal oxide feeds – with the small-scale isocyanates catalysts, surfactants and blowing agents largely neglected as very small-scale and except for blowing agents, without any major economic ties to feedstocks and low-cost utilities.

6.1 General

Polyurethane chemical production is in three or more stages, often at quite different facilities – in scale and philosophy:

- a) Production of isocyanates – MDI (methyl di-isocyanate) being the high growth rate isocyanate and TDI (toluene di-isocyanate) being the lesser important, older and low growth rate one. However, there are over 10 other isocyanates on the market to fit specialty markets.
- b) Production of propylene oxide and to a lesser extent (only insofar as isocyanates are concerned) ethylene oxide. Propylene glycols may also be produced at such a site; most Alberta ethylene oxide today is converted ethylene glycols.

The above isocyanate and propylene oxide facility types are lower volume (60 to 300 KTA) and/or high value added, continuous operations (somewhat similar to the operations Celanese is currently shuttering). Added ethylene oxide production is possible at one of Alberta's ethylene glycol plants, with over-the-fence supply.

- c) Production of polyols from propylene oxide, propylene glycols, ethylene oxide, ethylene glycols, other chemicals and sugar derivatives and/or similar compounds.

Polyol production is normally done in batch reactions – simple 10 atmospheres, 100 to 200°C stirred reactors, with steam or hot oil heating. A long series of polyols is usually produced for urethane and other markets served by the particular producer. As such, this is a specialty chemical operation akin, say, to operations at Prospec Chemicals.

- d) Polyurethane polymers are produced from MDI and/or TDI, selected polyols, catalysts, surfactants and other chemicals in small-scale at manufactures. The isocyanates (A package), polyols (B

package), and other ingredients are often provided by system house, rather than by major isocyanate manufactures.

6.2 Isocyanate Production

6.2.1 MDI Production

Economic MDI production in Alberta is seen as being, at least at a 100-KTA rate. The key benzene, ammonia, natural gas, formaldehyde feedstocks all appear available today, except for benzene, which continues in very tight supply.

While this study did not find the suitable benzene available today, new benzene supply is foreseen in almost all new Alberta chemical industry scenarios.

A 100-KTA MDI facility from the above feedstocks would cost in the order of \$400 to 600 million, with the final aniline to MDI steps very proprietary and likely those of the operator. Technologies for the other process steps to nitric acid, nitrobenzene, aniline, CO, and H₂ (from natural gas) area are generally available. This plant would be highly technical, with very tight environmental controls due to the nature of the feeds, intermediates and products. Staff levels will be in the 70 to 100 range.

It is to be noted that the MDI plant's product will be PMDI – liquid polymeric MDI with more or less MDI. Pure MDI might be produced via an added distillation step. Aniline is another potential merchant product, but also in low demand.

6.2.2 TDI Production in Alberta

TDI production in Alberta is seen only as an add-on to an MDI facility and only at a 50-KTA rate. Markets are disperse with few in Alberta/western Canada, hence, low cost production is essential. TDI is produced from toluene, ammonia (nitric acid), hydrogen and CO (from natural gas) – all but toluene being common to MDI production. Toluene will come available along with the new benzene supply.

The TDI facility would add \$100 to 120 million to the complex costs and add 30 to 40 personnel. Its economics greatly depend on the major synergies with nitric acid, synthesis gas utility and other auxiliary production MDI plant.

Promotion of TDI production in Alberta is seen only as an adjunct to a MDI facility.

6.2.3 Phosgene Route to Isocyanates?

While this study assumed new non-phosgene technologies to isocyanates for environmental and permitting reasons, a brief look at the conventional phosgene routes to MDI and TDI indicates a potential fit with revised or new ethylene dichloride production, which would use up the byproduct hydrochloric acid. (EDC potential was not examined in this study.)

6.3 Propylene Oxide/Ethylene Oxide

6.3.1 Propylene Oxide Production

Propylene oxide coproduction with styrene is one of the two current major routes to new styrene production. (Ethylene and benzene (for ethylbenzene) and propylene are the appropriate feedstocks in this route.) New styrene production interest was noted in the recent aromatics report and this interest appears to continue. An Alberta polyurethane chemicals industry could form an ideal outlet for much of the propylene oxide from such a POSM (or SMPO, depending on the operator) complex. This study did not re-examine the desire for such a complex, but notes its need and fair/good prospects for a major new benzene supply (which would also feed an MDI facility).

Degussa indicated interest in participating (with others) in a plant to use their hydrogen peroxide and Williams propylene in a new propylene oxide process with no byproducts. BASF recently announced plans for a 220-KTA plant, using BASF's process version.

Thus, local propylene demand is seen as the major need to develop local propylene oxide production. (Most propylene oxide plants also produce propylene glycols and often further derivatives.) Propylene is becoming available from Williams fractionation of a Suncor C₃ stream.

No estimates were made re propylene oxide production costs, nor staffing needs, due to the two quite different routes – but propylene oxide can be made available if a significant demand develops.

6.3.2 Ethylene Oxide

Ethylene oxide needs for polyols are not well defined at this time, but only added distillation may be needed. Location of the polyol production facility would best be fence line to existing ethylene glycol production.

Much more so than with propylene oxide markets, other than polyol should be promoted to encourage enhanced local merchant ethylene oxide production; again noting that land for its use should also be in the equation.

6.4 Polyol Production in Alberta

As note above, polyol production is usually smaller-scale, say, below 50-KTA and based on batch processing, with a wide variety of products made from a wide variety of feedstocks (including many chemicals not noted in this report). The range of products is usually set by the operator's specific market targets.

Sugars and derivatives are common ingredients. Alberta has sucrose and some sucrose-rich byproducts at Taber; it also has very large quantities of potato starch and some wheat starch as prospective glucose, etc. sources. Sorbitol and mannitol are made from sugars via hydrogenation. Research is needed to define the economics of each of these prospective sources to best suit a prospective polyol producer's product spectrum.

A polyol production facility "feels" likely if propylene oxide production is established here, but a polyol production facility is a relatively simple. A parallel start to sucrose, etc. facility would probably have continuous operation, but may best be located at the Alberta agriculture processing site of the feedstocks – e.g., Taber, Pincer Rutte or Red Deer.

REFERENCES

- a) The Alliance for the Polyurethane Industry, a business unit of the American Plastics Council, provides extensive data on the handling of polyurethane ingredients, with major emphasis on the isocyanates MDI and TDI.
- b) H. Gunardson's book "Industrial Gases in Petrochemical Processing" and his helpful comments, especially re phosgene or no phosgene routes in future MDI and TDI plants must be acknowledged.
- c) Many chemical company web sites provide extensive data on polyols and isocyanates – e.g., Dow Chemicals web site provides much information on their line of polyols.