

**BAT FOR LARGE VOLUME ORGANIC
CHEMICALS AND PRODUCTION
IN AUSTRIA**

BAT for Large Volume Organic Chemicals and Production in Austria

BE-183

Wien, Januar 2001

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Impressum

Medieninhaber und Herausgeber: Umweltbundesamt GmbH, Spittelauer Lände 5, A-1090 Wien
Eigenvervielfältigung

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ISBN 3-85457-572-6

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ZUSAMMENFASSUNG DES UMWELTBUNDESAMTES

Die vorliegende Studie behandelt angewandte Technologien, Einsatzstoffe, produktionsspezifische Emissionen und Ressourcenverbrauch in der Herstellung von organischen Grundchemikalien. Aufgrund der Vielfalt an organischen Verbindungen beschränkt sich die vorliegende Studie auf jene Verbindungen, die in Österreich in größeren Mengen hergestellt werden.

Die Studie wurde im Hinblick auf die EU – Richtlinie über „Integrierte Vermeidung und Verminderung der Umweltverschmutzung“ (RL 96/61/EG) und als Hilfestellung für die von der Europäischen Kommission errichtete „Technical Working Group“ über „Large Volume Organic Chemicals“ verfasst. Hierzu wurden jene österreichische Firmen, die in den Bereich der organischen Grundstoffchemie einzuordnen sind kontaktiert. Mit Hilfe von Fragebögen und Firmenbesuchen wurden die relevanten Informationen über die einzelnen Betriebe, die der organischen Grundstoffchemie in Österreich zuzuordnen sind, ermittelt. In der folgenden Zusammenfassung sind die wichtigsten, in Österreich hergestellten Produkte und verwendeten Prozesse angeführt.

Anschließend sind, in einer zusammenfassende Tabelle, die „Besten verfügbaren Techniken“ zur Reduktion von Luftschadstoffemissionen in der organischen Großchemie aus der Sicht des Umweltbundesamtes dargestellt. Diese Tabelle wurde aufgrund von Erfahrungen mit österreichischen Anlagen und eines Vergleichs einschlägiger Fachliteratur erstellt.

Abschließend ist in der vorliegenden Studie, die für den Bereich der organischen Chemie in Österreich relevante Gesetzeslage dargestellt, wobei sowohl Bestimmungen für die Bereiche der Luft- und Abwasseremissionen, als auch für den Bereich Abfall behandelt wurden. Weiters wurde auch die deutsche TA – Luft in dieser Studie behandelt, da sie auch in Österreich von den Genehmigungsbehörden als Anleitung herangezogen wird, sofern es für bestimmte Bereiche keine österreichischen Regelungen gibt.

Ethylen und Propylen

In Österreich werden sowohl Ethylen, als auch Propylen durch „steam cracken“ hergestellt. Es gibt in Österreich eine Anlage mit einem jährlichen Input von etwa 1 100 000 t/a Naphtha, Flüssiggas und Ethan, aus denen etwa 350 000 t/a Ethylen und etwa 200 000 t/a Propylen hergestellt werden.

Das Rohmaterial wird zunächst in Spaltöfen unter Zugabe von Dampf und unter Zufuhr von Energie in niedrigere Kohlenwasserstoffe gespalten. In den nachfolgenden Trennkolonnen werden unter anderem die Produkte Ethylen und Propylen separat abgetrennt. Weitere separat abgetrennte Ströme sind das Pyrolysebenzin, die C₄ Fraktion (zur Weiterverarbeitung siehe Abschnitt 1,3 – Butadien), Wasserstoff und Ethan.

Relevante Emissionen entstehen aus den Spaltöfen durch die Energiebereitstellung für die Spaltung der höheren organischen Verbindungen. In diesem Zusammenhang zu erwähnen sind NO_x, CO, CO₂, SO₂ und Staub. Als Brennstoff wird in den Spaltöfen Raffineriegas verwendet.

Abwasser entsteht bei der Entfernung der sauren Bestandteile aus den Spaltgasen durch Wäsche mit NaOH. Die mit Natriumsulfid beladene Ablauge wird in weitere Folge in einer Ablaugeoxidationsanlage zu Natriumsulfit und Natriumsulfat oxidiert und anschließend in einer Abwasserreinigungsanlage behandelt.

1,3 Butadien

Butadien wird in Österreich an einem Standort hergestellt. Die Kapazität dieser Anlage liegt bei 48 000 t/a, während die Jahresproduktion zwischen 40 000 und 45 000 Tonnen liegt.

Zur Herstellung von Butadien wird die C₄ Fraktion aus dem Steamcracker (siehe auch Ethylen und Propylen) verwendet. Die Abtrennung von Butadien aus diesem Gemisch von bis zu zwölf verschiedenen Kohlenwasserstoffen mit 4 Kohlenstoffatomen erfolgt in der österreichischen Anlage durch Extraktivdestillation. Als Extraktionsmittel wird N – Methylpyrrolidon (NMP) verwendet.

Die nach der Abtrennung von Butadien verbleibende C₄ Fraktion, die vor allem aus Isobuten, anderen Butenen und Butanen besteht, wird zur Herstellung von MTBE verwendet.

Acetylen

Die Produktion von Acetylen kann auf zwei grundsätzlich verschiedene Arten durchgeführt werden. Einerseits kann Acetylen durch nichtkatalytische Pyrolyse von Kohlenwasserstoffen erzeugt werden. Dabei kann ein weiter Bereich an Kohlenwasserstoffen als Rohmaterial eingesetzt werden. Andererseits besteht die Möglichkeit der Verwendung von Kalziumkarbid und Wasser als Rohmaterialien. In der vorliegenden Studie wird nur die zweite Möglichkeit genauer betrachtet, weil in Österreich sechs Anlagen existieren, die Acetylen auf Basis von Kalziumkarbid herstellen. Die Gesamtjahresproduktion dieser sechs Anlagen liegt allerdings unter 2000 Tonnen.

Bei der Verwendung von Kalziumkarbid als Ausgangsstoff entsteht in einer exothermen Reaktion aus Kalziumkarbid und Wasser Acetylen und das Nebenprodukt Kalkhydrat. Zur Reinigung des Acetylens werden meist dreistufige Wäscher verwendet, wobei beladene Schwefelsäure und Natronlauge als Reststoffe anfallen. Auch die Verwendung von zweistufigen Wäscher ist möglich. In den meisten Fällen werden die verbrauchten Waschlösungen von den Lieferanten wiederaufbereitet.

Das Nebenprodukt Kalkhydrat, das in großen Mengen anfällt, kann in den verschiedensten industriellen Bereichen eingesetzt werden. Beispielhaft seien die Zementindustrie, die Abwasserbehandlung, die Verwendung zur Neutralisation in der chemischen Industrie oder die Verwendung zur Rauchgasreinigung (Abscheidung von SO₂ und sauren Abgasbestandteilen) in kalorischen Kraftwerken angeführt.

Formaldehyd

Es werden zwei verschiedene Prozesse zur Herstellung von Formaldehyd unterschieden. Einerseits wird die oxidative Dehydrierung von Methanol mit Hilfe von Silberkatalysatoren und andererseits die Oxidation von Methanol mit Hilfe von Eisenoxid/Molybdänoxid Katalysatoren angewandt.

Am einzigen österreichischen Standort wird die oxidative Dehydrierung verwendet. Die Kapazität dieser Anlage liegt bei 91 000 Tonnen pro Jahr, berechnet als 100 % Formaldehyd. Im Jahr 1998 wurden 83 600 Tonnen produziert, wofür 102 000 Tonnen Methanol als Rohmaterial benötigt wurden.

Nach der katalytischen Umsetzung von Methanol an den Silberkatalysatoren werden die Reaktionsgase rasch abgekühlt, um eine Zersetzung des gebildeten Formaldehyds zu verhindern. Die Abtrennung des Formaldehyds aus den Reaktionsgasen erfolgt durch Absorption mit Wasser.

Das nach der Abtrennung von Formaldehyd anfallende Prozessabgas wird auf zwei unterschiedliche Arten behandelt. Etwas mehr als ein Drittel wird in Dampfkesseln zur Dampfer-

zeugung verbrannt. Der Rest wird in vier Gasmotoren zur Erzeugung von elektrischem Strom verwendet. Zusätzlich zur produzierten elektrischen Energie wird auch die Abwärme aus dem Abgas der Gasmotoren zur Dampferzeugung genutzt. Zur Minderung der Emissionen aus den Gasmotoren sind diese mit katalytischen Nachverbrennungseinrichtungen ausgestattet, in denen vor allem die Konzentrationen von CO und H₂ gesenkt werden.

Methyl – Tertiär – Butyl – Ether (MTBE)

Für die kommerzielle Produktion von MTBE werden drei verschiedene Verfahren eingesetzt. Zwei Verfahren verwenden Isobutan als Ausgangsmaterial. Das bedeutendste Verfahren verwendet Isobuten.

Auch in der einzigen österreichischen Anlage wird MTBE aus Isobuten hergestellt. Wie bereits beschrieben (siehe 1,3 Butadien) wird die von Butadien befreite C₄ Fraktion aus dem Steamcracker, die vor allem aus Isobuten, anderen Butenen und Butanen besteht verwendet. Weiters wird die olefinische C₄ Fraktion aus dem katalytischen Cracker der Raffinerie als Ausgangsmaterial verwendet, die ebenfalls Isobuten enthält. Das MTBE entsteht aus der Reaktion von Isobuten und Methanol. Die Auftrennung der Produktmischung MTBE, Methanol und verbleibende C₄ Fraktion ist schwierig, weil die Bestandteile azeotrope Mischungen bilden

Die Kapazität der österreichischen Anlage beträgt 67 000 t/a, wobei die Jahresproduktion zwischen 50 000 und 60 000 Tonnen liegt. Die verbleibende C₄ Fraktion (Raffinate 2, mit den anderen Butenen und Butanen) wird in Österreich als Mischkomponente für den Ottokraftstoff oder als Eingangsmaterial für den Steamcracker verwendet.

Maleinsäureanhydrid

Für die Produktion von Maleinsäureanhydrid können drei verschiedene Rohstoffe herangezogen werden, wobei die Verwendung von Benzol als Ausgangsstoff in den letzten Jahren sehr stark abnahm, was aus ökologischen Gründen besonders zu begrüßen ist. Die beiden anderen Ausgangsmaterialien die zurzeit Verwendung finden sind Butan und Buten, die durch Oxidation zu Maleinsäureanhydrid umgewandelt werden.

Am einzigen österreichischen Standort, an dem zwei Anlagen betrieben werden, wird seit 1994 ausschließlich Butan als Ausgangsstoff eingesetzt. Die Jahresproduktion der beiden Anlagen liegt bei etwa 26 000 t/a wofür in etwa 39 200 Tonnen Butan benötigt werden.

Zur Produktion des Maleinsäureanhydrids kommen am österreichischen Standort zwei verschiedene Prozesse zur Anwendung. In einer Anlage wird ein Wirbelschichtreaktor verwendet, während die zweite Anlage einen Festbettreaktor verwendet. Nach den Reaktoren wird aus der abgeschiedenen Maleinsäure in der Dehydriereinheit Maleinsäureanhydrid hergestellt. Die Dehydriereinheit wird von beiden Anlagen gemeinsam verwendet.

In der Wirbelschichtanlage werden die Prozessabgase nach Abtrennung des Maleinsäureanhydrids durch Absorption in Wasser in der Form von Maleinsäure einer Nachverbrennung zugeführt. Die Abwärme der nachverbrannten Prozessabgase wird zur Dampferzeugung verwendet.

Die Prozessabgase des Festbettprozesses werden in einer regenerativen Nachverbrennung behandelt. Zusätzlich zu den Prozessabgasen werden in dieser neuen regenerativen Nachverbrennung auch Xylolemissionen aus verschiedenen Quellen der Dehydriereinheit nachbehandelt, die bislang unbehandelt emittiert wurden. Die Abwärme der regenerativen Nachverbrennung wird derzeit nicht genutzt.

Das entstehende Abwasser (~ 4 m³/h) der beiden Maleinsäureanhydridanlagen wird in der zentralen Kläranlage des Standorts behandelt.

Phthalsäureanhydrid (PSA)

Zur Produktion von Phthalsäureanhydrid (PSA) werden zwei verschiedene Rohstoffe verwendet, wobei die Bedeutung von Naphthalin in letzter Zeit stark abnahm und heute der überwiegende Teil aus o – Xylol hergestellt wird. Auch in der österreichischen Anlage wird o – Xylol als Rohmaterial verwendet.

Die Kapazität der österreichischen Anlage beträgt 50 000 t/a. Für die Jahresproduktion, die zwischen 40 000 und 47 000 t/a liegt, werden zwischen 36 000 und 44 000 Tonnen o – Xylol benötigt.

Die Oxidation des o – Xylols zum PSA erfolgt katalytisch. Zur Abtrennung des gebildeten Phthalsäureanhydrids werden Kristallisatoren verwendet in denen das PSA aus den Reaktionsgasen auskondensiert wird. Diese Kristallisatoren werden abwechselnd gekühlt (zur Kristallisation) und beheizt (zum Entfernen des auskristallisierten PSAs).

Die wichtigsten Schadstoffe und Nebenprodukte, die nach der Abtrennung des PSAs im Abgas verbleiben sind organische Säuren (vor allem Maleinsäure), Kohlenmonoxid, o – Xylol und Schwefeldioxid, das zugegeben wird um die Ausbeute der Reaktion zu erhöhen, wenn keine neuen Katalysatoren verwendet werden.

In der österreichischen Anlage werden zur Reinigung dieses Abgases Gegenstromwäscher verwendet, wobei das Washwasser solange rezirkuliert wird, bis die Konzentration von Maleinsäure im Washwasser so hoch ist, dass die Waschlösung als Ausgangsstoff für andere Produktionsprozesse (z. B. Produktion von Fumarsäure) verwendet werden kann. Der Nachteil der Verwendung von Wäschern zur Abgasreinigung besteht darin, dass die hohe CO Konzentration (~ 7 000 mg/Nm³) und auch die aliphatischen Komponenten im Abgas nicht reduziert werden können.

Eine Alternative zu den oben beschriebenen Wäschern zur Abgasreinigung liegt in der Verwendung von thermischen oder katalytischen Nachverbrennungseinrichtungen, wodurch insbesondere die hohen Konzentrationen an CO reduziert werden können. Die Nachteile der Nachverbrennungseinrichtungen bestehen darin, dass keine Maleinsäure als Nebenprodukt gewonnen werden kann und, dass das Abgas, das nach der Abtrennung von PSA etwa 60 °C besitzt, zur Oxidation aufgeheizt werden muss.

Die effektivste Methode zur Rückgewinnung und zur Emissionsverringerung wäre die Kombination eines Wäscher mit einer katalytischen Nachverbrennung, wobei allerdings das feuchte, abgekühlte Abgas für die katalytische Nachverbrennung ebenfalls wieder aufgeheizt werden müsste.

Glyoxylsäure

Die Produktion von Glyoxylsäure kann durch verschiedene Prozesse erfolgen. Einerseits kann Glyoxylsäure durch Oxidation verschiedener Ausgangsstoffe wie beispielsweise Glyoxal, Acetaldehyd oder Ethylen hergestellt werden, wobei Salpetersäure als Oxidationsmittel verwendet wird. Andererseits besteht auch die Möglichkeit der Herstellung durch Ozonolyse von Maleinsäureanhydrid.

In Österreich wird Glyoxylsäure an einem Standort in drei Anlagen durch Ozonolyse hergestellt. Zwei dieser Anlagen stellen ausschließlich Glyoxylsäure her, während die dritte Anlage eine Ozonmehrproduktanlage darstellt, die außer Glyoxylsäure weitere Ozonolyseprodukte

herstellt. Die Gesamtkapazität dieser drei Anlagen an Glyoxylsäure liegt bei 14 990 t/a 50 %ige Glyoxylsäurelösung.

Die Prozessabgase aller drei Anlagen werden gemeinsam einer thermischen Nachverbrennung zugeführt. Weiters werden in dieser thermischen Nachverbrennung Erdgas, flüssige Reststoffe, belastete Lösungsmittel und Destillationsrückstände aus den Ozonolyseanlagen verbrannt. Weitere Rückstände der Ozonolyseanlagen werden in einer separaten Reststoffverbrennungsanlage unter Zugabe von Erdgas als Zusatzbrennstoff verbrannt.

Harnstoff

Zur Herstellung von Harnstoff werden eine Reihe verschiedener Prozesse verwendet. Allen gemeinsam sind die Ausgangsmaterialien, nämlich CO_2 und NH_3 . In der einzigen österreichischen Anlage, die eine Kapazität von 1 400 t/d und eine jährliche Produktion von etwa 400 000 t/a besitzt wird der SNAM – Progetti Prozess verwendet. Zur Herstellung einer Tonne Harnstoff werden 567 kg Ammoniak und 735 kg Kohlendioxid benötigt.

Im ersten Reaktionsschritt bilden Ammoniak und Kohlendioxid eine Ammoniumkarbamatlösung, die im zweiten Reaktionsschritt der Dehydratisierung zu Harnstoff und Wasser umgewandelt wird. Da die Ausbeute von Harnstoff gering ist (~ 62 %) muss die restliche Karbamatlösung, die in der ersten Reaktionsstufe aus NH_3 und CO_2 gebildet wurde, wieder gespalten und als CO_2 und NH_3 in den Reaktor zurückgeführt werden.

Nach der Spaltung und Rückführung der nicht umgesetzten Karbamatlösung wird das Prozesswasser, das bei der Dehydratisierungsreaktion anfällt ($300 \text{ kg/t}_{\text{Harnstoff}}$) in Vakuumverdampfern aus der Harnstofflösung abgetrennt.

Damit das Prozesswasser an die Umwelt abgegeben werden kann muss es behandelt werden. Einerseits wird der im Prozesswasser enthaltene Harnstoff durch Dampfwäsche entfernt. Ammoniak der ebenfalls im Prozesswasser enthalten ist wird durch Destillation abgetrennt. Das so behandelte Abwasser wird täglich analysiert und ins Fließwasser abgegeben (COD = 52 mg/l, NH_3 = 66 mg/l und Harnstoff = 186 mg/l).

Zur Verfestigung der konzentrierten Harnstofflösung nach dem Abtrennen des Prozesswassers können zwei Möglichkeiten, nämlich Granulation oder wie in der österreichischen Anlage ein Prillturm verwendet werden.

Zur Reinigung der Abgase aus dem Prillturm, die vor allem mit Harnstoff und Ammoniak belastet sind, werden in der österreichischen Anlage Wäscher verwendet. Mit diesen Wäschern werden Konzentrationen von $< 20 \text{ mg/Nm}^3$ sowohl für Ammoniak als auch Staub (Harnstoff) erreicht und somit die Grenzwerte, die jeweils bei 30 mg/Nm^3 liegen sicher eingehalten.

Pro Stunde fallen aus diesen Wäschern etwa 300 – 400 l konzentrierte Waschlösung an. Aufgrund des hohen Ammoniumnitratgehalts kann diese Waschlösung nicht in der Harnstoffproduktion wiederverwendet werden. Stattdessen wird sie in der Düngemittelproduktion am selben Standort eingesetzt.

Melamin

Zur Produktion von Melamin kann entweder Dicyandiamid oder Harnstoff verwendet werden. Bei der Verwendung von Harnstoff als Ausgangsmaterial unterscheidet man zwischen Hochdruckprozessen und katalytischen Niederdruckprozessen.

Am einzigen österreichischen Standort werden drei Anlagen mit Harnstoff als Ausgangsmaterial nach einem katalytischen Niederdruckverfahren betrieben. Seit dem Jahr 2000 wird eine vierte Anlage betrieben, die einen nichtkatalytischen Hochdruckprozess, ebenfalls mit

Harnstoff als Ausgangsmaterial verwendet. Zu dieser Anlage liegen noch keine detaillierten Informationen vor.

Die Kapazität der drei katalytischen Anlagen beträgt 50 000 t/a. Für diese Menge an Melamin sind in etwa 160 000 Tonnen Harnstoff notwendig.

Das katalytische Niederdruckverfahren, das in Österreich verwendet wird ist ein zweistufiges Verfahren. In der ersten Stufe wird Harnstoff in einer endothermen Reaktion in Ammoniak und Isocyanensäure gespalten. Die, für diese endotherme Reaktion benötigte Energie wird über Salzerhitzer, die mit Erdgas befeuert werden bereitgestellt, wobei vor allem NO_x und CO_2 als Schadstoffe auftreten.

In dem zweiten Reaktor wird Melamin katalytisch mit Hilfe von Al_2O_3 Katalysatoren gebildet. Die gebildeten Melamindämpfe werden anschließend gequenchet, zentrifugiert und getrocknet.

Die produzierten Nebenprodukte Ammoniak und Kohlendioxid werden in einem mehrstufigen Wäscher getrennt, wobei der reine Ammoniak (7 t/h) wiederverwendet wird. Das pure CO_2 wird nur teilweise benötigt. Der nicht benötigte Teil an CO_2 wird an die Umgebung abgegeben.

Außer den Emissionen aus der Energiebereitstellung stellen die Prozessabgase eine weitere Emissionsquelle dar. Zur Verringerung der Ammoniakkonzentration in ihnen wird ein zweistufiger Gegenstromwäscher verwendet. Die Ammoniakkonzentration kann durch diese Wäscher von $\sim 25\,000\text{ mg/Nm}^3$ im Eingang auf deutlich weniger als 30 mg/Nm^3 im Ausgang gesenkt werden.

Das Abwasser der drei Melaminanlagen wird in einer Abwasserbehandlungsanlage behandelt. Diese Abwasserbehandlungsanlage verwendet einen thermischen Hydrolysereaktor der Verunreinigungen, Nebenprodukte und Melamin in NH_3 und CO_2 spaltet, die anschließend durch Destillation getrennt und in die NH_3/CO_2 Trennstufe des Prozesses zurückgeführt werden.

Best verfügbare Techniken

Tabelle 1: BAT und assoziierte Emissionswerte für die Produktion von organischen Grundchemikalien¹

	Technologie	BAT Werte	Referenzen	Anmerkung
Rückgewinnung / Abscheidung von VOC	Selektive Membran Separation	90 – > 99 % [CONCAWE, 2000] 99 – 99.9 % Rückgewinnung [INFOMIL, 1999]	[1. Draft BRef WW & WGT, 2000a] [1. Draft BRef Refineries, 2000]	indikativer Anwendungsbereich 1 – > 10 g _{voc} /m ³
	Kondensation	Kondensation: 50 – 98 % [UK EA, 1999] + zusätzliche Abscheidung Tiefemperaturkondensation: 95 – 99 % [UK EA, 1999] 99.8 – 99.95 % Rückgewinnung [INFOMIL, 1999]	[1. Draft BRef LVOC, 2000a] [1. Draft BRef WW & WGT, 2000a] [1. Draft BRef Refineries, 2000]	indikativer Anwendungsbereich für Kondensation Menge 100 – > 100 000 m ³ /h 50 – > 100 g _{voc} /m ³ für Tiefemperaturkondensation: Menge 10 – 1000 m ³ /h 20 – 100 g _{voc} /m ³ 20 mbar – 6 bar
	Adsorption	95 – 99 % [UK EA, 1999] ² 99.95 – 99.99 % Rückgewinnung [INFOMIL, 1999]	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000] [1. Draft BRef WW & WGT, 2000a]	indikativer Anwendungsbereich für regenerative Adsorption Menge 100 – > 100 000 m ³ /h 0.01 – 10 g _{voc} /m ³ , 1 – 20 atm nicht regenerative Adsorption: Menge 10 – > 1000 m ³ /h 0.01 – 1.2 g _{voc} /m ³
Abscheidung von VOC	Wäscher	95 – 98 % Reduktion [UK EA, 1999] 99 – 99.95 % Reduktion [INFOMIL, 1999]	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000] [UBA, 2000a]	indikativer Anwendungsbereich Menge 10 – 50 000 m ³ /h 0.3 – > 5 g _{voc} /m ³

¹ Wenn nicht anders angegeben beziehen sich alle BAT Konzentrationen auf Standardbedingungen (trockenes Abgas bei 0 °C und 101.3 kPa) und einen Sauerstoffgehalt von 3 Vol. %, Halbstundenmittelwerte

² für nicht regenerative Adsorption 90 – 99 %

	Technologie	BAT Werte	Referenzen	Anmerkung	
Abscheidung von VOC	Thermische Verbrennung	99 % Reduktion [UK EA, 1999] 99.8 – 99.99 % Reduktion [INFOMIL, 1999] VOC ³ < 1 – 20 mg/m ³	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000]	indikativer Anwendungsbereich Menge 1000 – 100 000 m ³ /h 0.2 – > 10 g _{VOC} /m ³ Der Wert von 1 – 20 mg/m ³ basiert auf Emissionsgrenzwerten und gemessenen Emissionskonzentrationen von 5 österreichischen Anlagen ⁴	
	Katalytische Verbrennung	99 % Reduktion [UK EA, 1999] 95 – 99 % Reduktion [INFOMIL, 1999] VOC ³ < 1 – 20 mg/m ³	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000] [1. Draft BRef WW & WGT, 2000a]	indikativer Anwendungsbereich Menge 10 – 100 000 m ³ /h 0.05 – 3 g _{VOC} /m ³	
	Fackeln	Hochfackeln > 99 % Bodenfackeln > 99.5 %	[UBA, 2000a] [1. Draft BRef WW & WGT, 2000b]		
	Abscheidung von Partikeln	Zyklon	< 95 % Reduktion ⁵	[1. Draft BRef WW & WGT, 2000c]	Zyklone sind nur in Kombination mit einer anderen Abscheidetechnik als BAT anzusehen
		Elektrofilter ⁶	5 – 15 mg/Nm ³ 99 – 99.9 % Reduktion	[1. Draft BRef Refineries, 2000] [UBA, 2000b]	
		Faserfilter ⁶	< 5 mg/Nm ³	[1. Draft BRef Refineries, 2000] [UBA, 2000b]	

³ Die Abscheiderate von regenerativer oder rekuperativer Verbrennung kann kleiner als 99 % sein, aber der vorgeschlagene BAT Wert von < 20 mg/Nm³ kann auch mit diesen Technologien erreicht werden.

⁴ Die verschiedenen Anlagen sind detailliert in diesem Bericht

⁵ hängt stark von der Partikelgröße ab

⁶ Es existieren viele Beispiele aus verschiedenen industriellen Bereichen, dass Elektrofilter und Faserfilter die oben angegebenen Werte erreichen können. (z. B. siehe BRef "Nichteisenmetalle".

	Technologie	BAT Werte	Referenzen	Anmerkung
Abscheidung von Partikeln	zweistufiger Staubfilter	~ 1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000d]	
	Keramikfilter	< 1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000e]	
	Absoluter Filter	< 0.1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000f]	
	HEAF Filter	Tröpfchen bis zu 99 % Aerosole bis zu 99 %	[1. Draft BRef WW & WGT, 2000g]	
	Mist Filter	Staub bis zu 99 % Aerosole bis zu 99 %	[1. Draft BRef WW & WGT, 2000h]	
	Adsorption	80 – 95 % Reduktion für Geruchsstoffe	[1. Draft BRef WW & WGT, 2000i]	indikativer Anwendungsbereich 10 000 – 200 000 ou/Nm ³
Reduktion von Geruchsbelästigungen	Biofilter	75 – 95 % Reduktion für Geruchsstoffe ⁷	[1. Draft BRef WW & WGT, 2000j]	indikativer Anwendungsbereich 20 000 – 200 000 ou/Nm ³
	feuchte Kalkwäsche	90 – 97 % Reduktion SO ₂ < 100 mg/Nm ³	[BRef Cement & Lime, 2000] [BRef Glass, 2000]	
Abscheidung von SO ₂ und sauren Gasen	Wäscher	HCl ⁸ < 10 mg/Nm ³ HBr ⁸ < 5 mg/Nm ³ HF < 1 mg/Nm ³	Grenzwerte aus Genehmigungen österreichischer Anlagen [1. Draft BRef WW & WGT, 2000k] [BRef Cement & Lime, 2000] [BRef Glass, 2000]	basischer Wäscher

⁷ bei einer Belastung des Abgases > 5 000 ou/Nm³

⁸ Die Konzentrationsangaben basieren auf Grenzwerten österreichischer Chemieanlagen (Tagesmittelwert bei Standardbedingungen; Halbstundenmittelwerte HCl < 30 mg/m³ and HBr < 10 mg/m³)

	Technologie	BAT Werte	Referenzen	Anmerkung
Abscheidung von SO ₂ und sauren Gasen	halbtrockene Sprühdabsorption	SO ₂ < 100 mg/Nm ³ HCl < 10 mg/Nm ³ HF < 1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000] [BRef Cement & Lime, 2000] [BRef Glass, 2000]	
Abscheidung von NO _x	SNCR	50 – 80 % NO _x Reduktion	[1. Draft BRef WW & WGT, 2000m] [BRef Cement & Lime, 2000] [BRef Glass, 2000]	
	SCR	85 – 95 % Reduktion NO _x < 50 mg/m ³ NH ₃ < 5 mg/m ³	die erreichbaren Konzentrationen basieren auf Angaben in [1. Draft BRef LVOC, 2000b]	
Reduktion von Dioxin-emissionen	Primärmaßnahmen + Adsorption	< 0.1 ng TEQ/Nm ³	[UBA, 2000c]	Die Dioxinbildung soll soweit wie möglich verhindert werden
Abscheidung von Quecksilber	Adsorption	0.05 mg/Nm ³	[1. Draft BRef WW & WGT, 2000]	< 0.01 mg/Nm ³ werden in österreichischen Müllverbrennungsanlagen gemessen
Abscheidung von Ammoniak ⁹ and Aminen	Wäscher	< 1 – 10 mg/Nm ³	[1. Draft BRef WW & WGT, 2000k]	sauerer Wäscher
Abscheidung von H ₂ S	Adsorption	80 – 95 % Reduktion 1 – 5 mg/Nm ³	[1. Draft BRef WW & WGT, 2000] Grenzwert aus einer österreichischen Anlageneignung	

⁹ Eine Melaminanlage in Österreich hat einen Grenzwert von 30 mg NH₃/Nm³ Halbstundenmittelwert und erreicht in etwa 6 mg/Nm³ Jahresmittelwert bei 25 000 mg NH₃/Nm³ im Rohgas bei einem Abgasvolumenstrom von 8000 Nm³/h

SUMMARY OF THE FEDERAL ENVIRONMENT AGENCY

This study deals with the applied technologies, input materials and emissions specific for the production of "Large Volume Organic Chemicals". It has been written in order to describe the state of art for the production of organic chemicals, which are produced in Austria.

The study was drawn up in view of the EU directive on "Integrated Pollution Prevention and Control" (96/61/EC) and is supposed to support the "Technical Working Group" on Large Volume Organic Chemicals, which was established by the European Commission. For this purpose Austrian companies, which produce organic base chemicals have be contacted by the Federal Environment Agency. On the following pages relevant information about the main products and processes are summarised.

Additionally a Table summarise the "Best Available Techniques" for the reduction of air emissions of different pollutants. This list of techniques is based on experiences of Austrian plants and a comparison of relevant literature.

The last chapter of this study deals with relevant legislation for the organic chemistry in Austria. Legislation for air and water emissions as well as legislation for waste is described in this Chapter. Additionally to the Austrian legislation the German TA – Luft is described in this study, because it is used as a guideline by the Austrian permitting authorities for substances where no Austrian regulations do exist.

Ethylene and Propylene

In Austria ethylene a well as propylene are produced at one steam cracker. From an annual input of 1 100 000 tonnes naphtha, LPG¹⁰ and ethane approximately 350 000 t/a ethylene and approximately 200 000 t/a propylene are produced.

In the first step the raw materials, mixed with steam are cracked in the cracking furnaces into lower hydrocarbons. In the following separation columns the different products are separated. Beside ethylene and propylene, pyrolysis petrol, a C₄ fraction (for further treatment of this fraction see 1,3 butadiene), hydrogen and ethane are separated in the separation columns.

Relevant emissions occur in the cracking furnaces, which produce energy that is necessary for the cracking of the higher hydrocarbons. Important pollutants of these furnaces are NO_x, CO, CO₂, SO₂ and dust. The cracking furnaces in Austria use refinery gas as fuel.

Waste water is produced during the separation of the acid gases from the cracking gases with caustic soda. The formed waste lye, which is loaded with sodium sulphide is subsequently oxidised in a waste lye oxidation plant to form sodium sulphate and sulphite and after the oxidation further treated in a waste water treatment plant.

1,3 Butadiene

Butadiene is produced at one location in Austria. The capacity of this plant is 48 000 t/a. The annual production is between 40 000 and 45 000 tonnes.

For the production of butadiene the C₄ fraction of the steam cracker (see ethylene and propylene) is used. The separation of butadiene from this mixture of up to twelve different hydrocarbons with four carbon atoms is made by extractive distillation in Austria. The solvent used in the Austrian plant is N-methylpyrrolidone (NMP).

¹⁰ LPG...Liquefied Petroleum Gas

The remaining C₄ fraction (after the separation of butadiene) mainly consists of isobutene, other butenes and butanes and is used for the production of MTBE.

Acetylene

The production of acetylene can be divided into two completely different groups. One part of the processes uses calcium carbide as raw material, whereas different thermal processes manufacture acetylene by pyrolysis of different hydrocarbons. In this study only the production from calcium carbide and water is described in detail, because six plants in Austria produce acetylene by using this technology. The annual production of these six plants together is lower than 2 000 tonnes.

Calcium carbide and water react in an exothermic reaction and form acetylene. The main by – product of this reaction is lime hydrate. In most of the cases three staged scrubbers are used for cleaning the produced acetylene. Also the use of two staged scrubbing systems is possible. In these scrubbers waste sulphuric acid and waste caustic soda are produced. In most of the cases these used washing solutions are regenerated by the supplier.

The by – product lime hydrate, which is produced in large amounts can be used in various applications. Examples are the cement industry, waste water treatment, the use in the chemical industry as neutralising agent or the use in the flue gas cleaning systems of power plants to abate SO₂ and other acidic components of the exhaust gas (e. g. HCl).

Formaldehyde

The production processes of formaldehyde can be divided into two groups due to the type of chemical reaction which is used. On the one side formaldehyde is produced with oxidative dehydrogenation of methanol on silver catalysts. The other possibility is the oxidation of methanol on iron oxide/molybdenum oxide catalysts.

The only Austrian plant uses oxidative dehydrogenation. The capacity of this plant is 91 000 tonnes per year calculated as hundred percent formaldehyde. This corresponds to a capacity of 250 000 tonnes per year related to a formaldehyde solution with 36.5 % formaldehyde. The annual production in 1998 was 83 600 tonnes of formaldehyde (100 %) or 229 000 tonnes of formaldehyde (36 %). For the production of these amounts of formaldehyde 102 000 tonnes methanol were used in 1998.

After the catalytic conversion of methanol at the silver catalysts to formaldehyde the reaction gases are immediately cooled down to avoid the decomposition of the formed formaldehyde. For the separation of formaldehyde from the reaction gases absorption with water is used.

After the separation of formaldehyde process exhaust gas remains, which is a relevant source of emissions. This exhaust gas is treated in two different ways at the Austrian plant. Approximately one third of the exhaust gas is incinerated in steam boilers and therefore used for steam production. The rest of the exhaust gas (~ 2/3) is used for the production of electricity in four gas engines. Additionally the waste heat of the combustion in the gas engines is also used for steam production. To minimise the emissions of the gas engines each engine has an exhaust gas catalytic converter, especially to oxidise the CO in the exhaust gas.

Methyl – Tertiary – Butyl – Ether (MTBE)

For the commercial production of MTBE three different processes are used. Two processes use isobutane as raw material. The most important process uses isobutene as raw material.

Also the only Austrian plant for MTBE production uses isobutene as raw material. As already described above (see 1,3 butadiene) the remaining C₄ fraction of the steam cracker after the separation of butadiene is used. This fraction mainly consists of isobutene, other butenes and butanes. Additionally the olefinic C₄ fraction from the FCC unit, which also contains isobutene is used as raw material in Austria.

MTBE is formed due to the reaction of isobutene and methanol. The separation of the product mixture, which consists of MTBE, methanol and the remaining C₄ fraction is very difficult because these components form an azeotropic mixture.

The capacity of the Austrian plant is 67 000 t/a. The annual production varies between 50 000 and 60 000 tonnes. The remaining C₄ fraction (Raffinate 2), mainly containing the other butenes and butanes is used as blending component for gasoline production or as feed material for the steam cracker.

Maleic Anhydride

For the production of maleic anhydride three different raw materials can be used, but the use of benzene as raw material decreased sharply in the last years. The two other raw materials which gained in importance in the last years are butane and butene.

At the only Austrian location two plants produce maleic anhydride. Since 1994 only butane is used as raw material. The annual production of the two plants is approximately 26 000 t/a. For this amount of maleic anhydride 39 200 tonnes butane are necessary. Two different processes are used in these plants.

One process uses a fluidized bed reactor, whereas the other process uses a fixed bed reactor for the oxidation of butane to maleic anhydride. For the separation of the maleic anhydride from the process gases absorption with water is used and maleic anhydride is precipitated in the form of maleic acid. In the next step the precipitated maleic acid is dehydrated to maleic anhydride in the dehydration unit. This dehydration unit is used together from both processes.

The process exhaust gas of the fluidised bed process is incinerated and used for steam production. The waste heat of this incinerator is used for steam production.

The process exhaust gas of the fixed bed reactor is treated in a regenerative firing. Additionally to the process exhaust gas of the fixed bed reactor this regenerative firing also treats the xylene emissions of different sources at the dehydration unit, which have been emitted without any treatment until now. The waste heat of this regenerative firing is currently not recovered.

The produced waste water (~ 4 m³/h) of the two plants is treated in the central waste water treatment plant of the location.

Phthalic Anhydride

Two different raw materials for phthalic anhydride production exist. The first possibility is the production from naphthalene, but the importance of naphthalene as raw material decreased in the last decades. Nowadays o-xylene is the major feedstock for phthalic anhydride production. Also the Austrian plant uses o-xylene as raw material.

The annual capacity of the only Austrian plants is 50 000 t/a. The annual production of this plant is between 40 000 and 47 000 tonnes. For this amount of phthalic anhydride between 36 000 and 44 000 tonnes xylene are necessary. The oxidation of o-xylene to phthalic anhydride is catalytic. For the separation of the phthalic anhydride from the reaction gases crystallizers are used.

The most important pollutants and by – products, which remain in the reaction gases after the separation of the phthalic anhydride are organic acids (especially maleic acid), carbon monoxide, o – xylene and sulphur dioxide, which is added before the reactor to improve the yield of the reaction if no new catalysts are used.

In the Austrian plant wet scrubbers with counter current flow are used to clean this exhaust gas. The washing solution is recirculated until the concentration of maleic acid in the washing solution is high enough for further use (e. g. for the production of fumaric acid). The disadvantage of scrubbers for exhaust gas cleaning in this process is that the high concentrations of carbon monoxide ($\sim 7\,000\text{ mg/Nm}^3$) can not be reduced with this technique.

An alternative to the above described scrubbers for exhaust gas cleaning is the use of thermal or catalytic incinerators. The high concentration of CO in the exhaust gas can be significantly reduced by using one of these techniques. The disadvantages are that the by – product maleic acid can not be recovered, because it is also incinerated and that the exhaust gas which has approximately $60\text{ }^\circ\text{C}$ after the separation of the phthalic anhydride has to be heated up for the oxidation.

The most effective method for recovery and emission reduction would be a combination of a scrubber with subsequent catalytic incineration. Again the disadvantage of this combination is that the moist and cold exhaust gas has to be heated up for the catalytic incineration.

Glyoxylic Acid

For the production of glyoxylic acid a few different processes exist. One possibility is the oxidation of different raw materials like glyoxal, acetaldehyde or ethylene. Nitric acid is used as oxidising agent for these oxidation reactions. An other possibility is the ozonolysis of maleic anhydride, which is used in Austria.

In Austria glyoxylic acid is produced at one location in three different plants. All three plants use the ozonolysis of maleic anhydride for the production glyoxylic acid. Two of these plants produce only glyoxylic acid, whereas the third plant is a multipurpose plant where other ozonolysis products are produced together with glyoxylic acid. The total capacity for glyoxylic acid of all three plants is $14\,990\text{ t/a}$ 50 % solution of glyoxylic acid.

The exhaust gases of all three plants are treated together in a thermal exhaust gas incinerator. Together with the exhaust gases of the three glyoxylic acid plants natural gas, liquid by – products of the ozonolysis plants, contaminated solvents of the ozonolysis plants and distillation residues of the ozonolysis plants are combusted in this incinerator. Further residues of the ozonolysis plants are incinerated together with natural gas in a separate incinerator.

Urea

For the production of urea a lot of different processes exist, but all different processes use the same raw materials (CO_2 and NH_3). The only Austrian plant, with a capacity of $1\,400\text{ t/d}$ and an annual production of approximately $400\,000$ tonnes uses the SNAM – Progetti process. For the production of one tonne urea 567 kg ammonia and 735 kg carbon dioxide are necessary.

In the first reaction stage ammonium carbamate is formed from ammonia and carbon dioxide. In the subsequent dehydration reaction urea and water are formed from the ammonium carbamate. The yield of urea is low ($\sim 62\%$) and therefore the rest of the carbamate solution is decomposed into CO_2 and NH_3 and recirculated to the reactor.

After the decomposition and recirculation of the unreacted carbamate solution, the process water, which is produced during the dehydration reaction ($\sim 300 \text{ kg/t}_{\text{urea}}$) is separated from the urea solution in two vacuum evaporators.

Before the separated process water can be discharged to the environment it has to be treated due the amount of urea and ammonia in it. To recover the urea in the process water vapour washing before condensation is used. Ammonia in the process water is separated and recovered by distillation. The treated process water is daily analysed and discharged to the running water (COD = 52 mg/l, NH_3 = 66 mg/l and urea = 186 mg/l).

After the separation of the process water two different methods for the solidification of urea exist. Most of the new plants use granulation, whereas older plants, like the Austrian plant mainly use prilling towers.

The most important pollutants in the exhaust gas from the prilling tower are urea and ammonia. The Austrian plant uses scrubbers to clean this exhaust gas. With these scrubbers concentrations of less than 20 mg/Nm^3 for both, ammonia and urea are achieved. The emission limits for ammonia as well as for urea are 30 mg/Nm^3 .

Between 300 and 400 l/h washing solution are discharged from these scrubbers. Due to the high concentration of ammonium nitrate in the discharged washing solution it can not be recycled to the urea production. Instead of this the solution is used in the fertilizer production at the same side.

Melamine

The most important raw materials for melamine production are urea and dicyandiamide. Processes that use urea as raw material can be distinguished into non – catalytic high pressure processes and catalytic low pressure processes.

At the only Austrian location three plants use a catalytic low pressure process with urea as raw material. Since 2000 a fourth plant using a non – catalytic high pressure process started with operation. Detailed information for this new plant, which is in the service trial are not available until now.

The capacity of the three other plants using the catalytic low pressure process is 50 000 t/a. For this amount of melamine approximately 160 000 tonnes urea are needed.

The catalytic low pressure process, which is used in the Austrian plants is a two staged process. In the first reactor urea is decomposed in an endothermic reaction to ammonia and isocyanic acid. The energy needed for this endothermic reaction is supplied by salt melting plants. These salt melting plants use natural gas as a fuel and the main pollutants of these plants are CO_2 and NO_x .

In the second reactor (fixed bed) melamine is formed with Al_2O_3 catalysts. After the formation the melamine vapour is quenched, centrifuged and dried.

During the production of melamine the by – products ammonia and carbon dioxide are formed, which are separated in a multi staged scrubber. The pure ammonia (7 t/h) is recycled to the ammonia storage facilities, whereas only part of the pure CO_2 is needed and therefore recycled. The rest is disposed of.

Beside the emission from the energy supply the process exhaust gases are an other relevant source of emissions. To decrease the ammonia concentration in these process gases a two staged counter current flow scrubber is used. The ammonia concentration is reduced with from $\sim 25 000 \text{ mg/Nm}^3$ in the inlet of the scrubber to significantly less than 30 mg/Nm^3 in the outlet of the scrubber (emission limit).

The waste water of all three melamine plants is treated in a waste water treatment plant. A thermal hydrolysis reactor is used to decompose several impurities, by – products and melamine in NH_3 and CO_2 , which are subsequently separated by distillation and recycled to the NH_3/CO_2 separation section of the process.

Best Available TechniquesTable 1: BAT and associated emission values for the production of Large Volume Organic Chemicals¹¹

	Technology	BAT Values	References	Remark
Recovery / Abatement of VOC	Selective Membrane Separation	90 – > 99 % [CONCAWE, 2000] 99 – 99.9 % Recovery [INFOMIL, 1999]	[1. Draft BRef WW & WGT, 2000a] [1. Draft BRef Refineries, 2000]	Indicative application range 1 – > 10 g _{voc} /m ³
	Condensation	Condensation: 50 – 98 % [UK EA, 1999] + additional abatement [UK EA, 1999] Cryo-condensation: 95 - 99 % [UK EA, 1999] 99.8 – 99.95 % Recovery [INFOMIL, 1999]	[1. Draft BRef LVOC, 2000a] [1. Draft BRef WW & WGT, 2000a] [1. Draft BRef Refineries, 2000]	Indicative application range for condensation: flow 100 – > 100 000 m ³ /h 50 – > 100 g _{voc} /m ³ for cryo-condensation: flow 10 – 1000 m ³ /h 20 – 100 g _{voc} /m ³ 20 mbar – 6 bar
Abatement of VOC	Adsorption	95 – 99 % [UK EA, 1999] ¹² 99.95 – 99.99 % Recovery [INFOMIL, 1999]	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000] [1. Draft BRef WW & WGT, 2000a]	Indicative application range for regenerative adsorption flow 100 – > 100 000 m ³ /h 0.01 – 10 g _{voc} /m ³ , 1 – 20 atm non regenerative adsorption flow 10 – > 1000 m ³ /h 0.01 – 1.2 g _{voc} /m ³
	Scrubbers	95 – 98 % Reduction [UK EA, 1999] 99 – 99.95 % Reduction [INFOMIL, 1999]	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000] [UBA, 2000a]	Indicative application range flow 10 – 50 000 m ³ /h 0.3 – > 5 g _{voc} /m ³

¹¹ If nothing else is stated all BAT concentrations are related to standard conditions (dry exhaust gas, 0 °C and 101.3 kPa) and an oxygen content of 3 Vol. %, half hourly

¹² for non regenerative adsorption 90 – 99 %

Technology	BAT Values	References	Remark
Abatement of VOC	99 % Reduction [UK EA, 1999] 99.8 – 99.99 % Reduction [INFOMIL, 1999] VOC ¹³ < 1 – 20 mg/m ³	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000]	Indicative Application range flow 1000 – 100 000 m ³ /h 0.2 - > 10 g _{voc} /m ³ The proposed level of 1 – 20 mg/m ³ is based on emission limits and measured values of 5 Austrian plants from 3 different branches of LVOC ¹⁴
	99 % Reduction [UK EA, 1999] 95 – 99 % Reduction [INFOMIL, 1999] VOC ³² < 1 – 20 mg/m ³	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000] [1. Draft BRef WW & WGT, 2000a]	Indicative application range flow 10 – 100 000 m ³ /h 0.05 – 3 g _{voc} /m ³
	elevated flares > 99 % ground flares > 99.5 %	[UBA, 2000a] [1. Draft BRef WW & WGT, 2000b]	
	< 95 % Reduction ¹⁵	[1. Draft BRef WW & WGT, 2000c]	Cyclones are only seen as BAT in combination with an other abatement techniques
	5 – 15 mg/Nm ³ 99 – 99.9 % reduction	[1. Draft BRef Refineries, 2000] [UBA, 2000b]	
Abatement of Particulates	< 5 mg/Nm ³	[1. Draft BRef Refineries, 2000] [UBA, 2000b]	

¹³ The reduction efficiency of regenerative or recuperative incinerators may be lower than 99 %, but the suggested BAT value of < 20 mg/Nm³ can be achieved with these technologies.

¹⁴ Included in the different branches are the production of formaldehyde, maleic anhydride and glyoxylic acid.

¹⁵ Strongly dependant on the particle size

¹⁶ There are a lot of examples that ESPs and Fabric filters can reach the values given above from different industrial branches. For examples see the BRef on "Non Ferrous Metals".

	Technology	BAT Values	References	Remark
Abatement of Particulates	Two stage dust filter	~ 1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000d]	
	Ceramic filter	< 1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000e]	
	Absolute Filter	< 0.1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000f]	
	HEAF Filter	droplets up to 99 % aerosols up to 99 %	[1. Draft BRef WW & WGT, 2000g]	
	Mist Filter	dust up to 99 % aerosols up to 99 %	[1. Draft BRef WW & WGT, 2000h]	
	Adsorption	80 – 95 % Reduction for odour	[1. Draft BRef WW & WGT, 2000i]	Indicative application range 10 000 – 200 000 ou/Nm ³
Odour	Biofilter	75 – 95 % Reduction for odour ¹⁷	[1. Draft BRef WW & WGT, 2000j]	Indicative application range 20 000 – 200 000 ou/Nm ³
	Wet limestone scrubbing	90 – 97 % Reduction SO ₂ < 100 mg/Nm ³	[BRef Cement & Lime, 2000] [BRef Glass, 2000]	
Abatement of SO ₂ and acid gases	Scrubbers	HCl ¹⁸ < 10 mg/Nm ³ HBr ³⁷ < 5 mg/Nm ³ HF < 1 mg/Nm ³	Permits of Austrian plants [1. Draft BRef WW & WGT, 2000k] [BRef Cement & Lime, 2000] [BRef Glass, 2000]	alkaline scrubbers

¹⁷ with a load of > 5 000 ou/Nm³

¹⁸ Concentrations are based on current permits of Austrian organic chemical plants (daily mean value at standard conditions; the half hourly values are HCl < 30 mg/m³ and HBr < 10 mg/m³)

	Technology	BAT Values	References	Remark
Abatement of SO ₂ and acid gases	Semi Dry Sorbent Injection	SO ₂ < 100 mg/Nm ³ HCl < 10 mg/Nm ³ HF < 1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000] [BRef Cement & Lime, 2000] [BRef Glass, 2000]	
Abatement of NO _x	SNCR	50 – 80 % NO _x reduction	[1. Draft BRef WW & WGT, 2000m] [BRef Cement & Lime, 2000] [BRef Glass, 2000]	
	SCR	85 to 95 % reduction NO _x < 50 mg/m ³ NH ₃ < 5 mg/m ³	The achievable emission concentration are based on values given in [1. Draft BRef LVOC, 2000b]	
Dioxins	Primary measures + Adsorption	< 0.1 ng TEQ/Nm ³	[UBA, 2000c]	generation of dioxins should be avoided as far as possible
Mercury	Adsorption	0.05 mg/Nm ³	[1. Draft BRef WW & WGT, 2000]	< 0.01 mg/Nm ³ measured at Austrian waste incineration plants
Ammonia ¹⁹ and amines	Scrubber	< 1 – 10 mg/Nm ³	[1. Draft BRef WW & WGT, 2000k]	Acid scrubber
H ₂ S	Adsorption	80 – 95 % reduction 1 – 5 mg/Nm ³	[1. Draft BRef WW & WGT, 2000] Permit of Austrian plant	

¹⁹ Melamin plant in Austria is permitted for 30 mg NH₃/Nm³ half hour mean value, achieving about 6 mg/Nm³ yearly average, raw gas: 25 000 mg NH₃/Nm³ , 8000 Nm³/h

1 INTRODUCTION

1.1 Objective of the Study

This study deals with the applied technologies, input materials, production specific emissions and resource consumption in the production of “Large Volume Organic Chemicals”. It has been written in order to describe the state of art for the production of organic chemicals which are produced in Austria.

The study was drawn up in view of the EU directive on “Integrated Pollution Prevention and Control” (96/61/EC) and is supposed to support the “Technical Working Group” on “Large Volume Organic Chemicals” which was established by the European Commission.

1.2 IPPC Directive

The European Commission organises according to Article 16.2 of the Council Directive 96/61/EC of 24 September 1996 concerning Integrated Pollution Prevention and Control (IPPC) the exchange of information between member states and the concerned industries on Best Available Techniques (BAT), associated monitoring and developments in them and to publish the results of the information exchange. The BAT documents for categories of industrial activities of annex I of the IPPC directive are made in Technical Working Groups, which are established under the umbrella of the Information Exchange Forum (IEF). The work of the Technical Working Groups is supported by the European Integrated Pollution Prevention and Control Bureau (EIPPCB), which is located within the IPTS (Institute for Prospective Technological Studies) in Seville, Spain.

The Kick off Meeting of the Technical Working Group for Large Volume Organic Chemicals took place in April 1999 in Seville.

Article 2.11 of the IPPC directive defines “Best Available Techniques” as follows: “Best Available Techniques” shall mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.

- “techniques” shall include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;
- “available” techniques shall mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;
- “best” shall mean most effective in achieving high general level of protection of the environment as a whole.

In determining the best available techniques special consideration should be given to the items listed in Annex IV of the Integrated Pollution Prevention and Control directive:

- the use of low waste technology;
- the use of less hazardous substances;

- the furthering of recovery and recycling of substances generated and used in the process and of waste, where appropriate;
- comparable processes, facilities or methods of operation which have been tried with success on an industrial scale;
- technological advances and changes in scientific knowledge and understanding;
- the nature, effects and volume of the emissions concerned;
- the commissioning dates for new or existing installations;
- the length of the time needed to introduce the best available techniques;
- the consumption and nature of raw materials (including water) used in the process and their energy efficiency;
- the need to prevent or reduce to a minimum the overall impact of the emissions on the environment and the risk to it;
- the need to prevent accidents and to minimise the consequences for the environment;
- the information published by the Commission pursuant to Article 16 (2) or by international organisations.

At the Kick off Meeting of the Technical Working Group for Large Volume Organic Chemicals the Structure of this BAT document was fixed. The document will be divided into three different parts. The first part describes general techniques. The most important second part deals with different sub-sectors of the chemical industry like lower olefins or oxygenated compounds. In the third part illustrative processes for the different sub-sectors will be described (e.g. cracking or formaldehyde production). A detailed structure of the BRef can be found in Figure 1.

According to the structure of the BRef this study will deal with organic chemicals produced in Austria that are within the scope of this document (see Chapter 1.3).

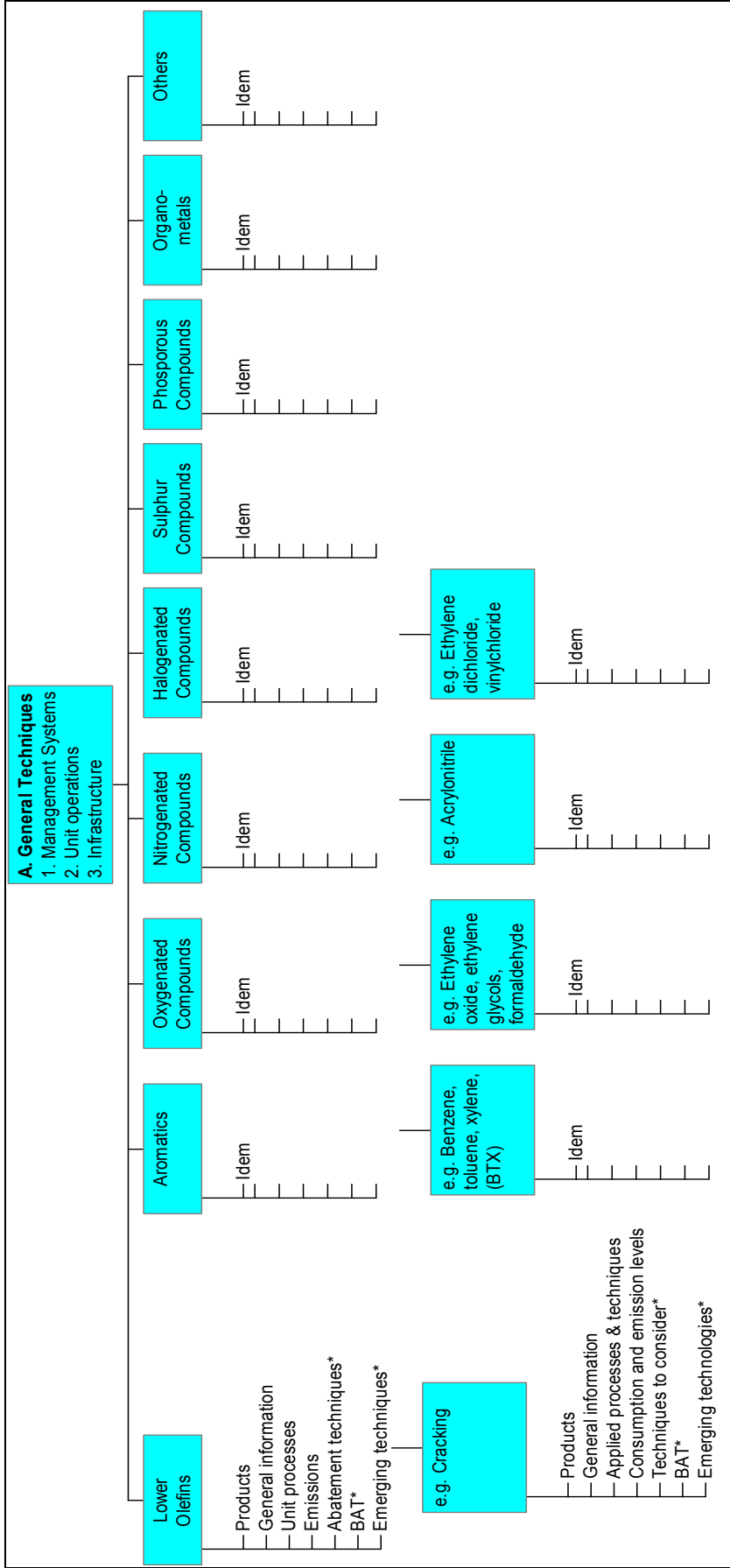


Figure 1: Structure of the BRef Large Volume Organic Chemicals [RADWAY, 1999]

1.3 The Chemical Industry

The contribution of the chemical industry to the European Community gross domestic products amounts for 2.4 %. Within the EC manufacturing industry chemistry ranks third in terms of value added and in terms of sales. In the European Community 36 000 chemical companies employ 1.7 million people (1998). Since 1990 the number of employees decreased by 14 %, whereas the production has grown from 1990 to 1998 by approximately 25 %. The production of large volume organic chemicals is an important part of the whole chemical industry with significant contribution to the above mentioned values.

The capacities of some important organic compounds are presented in Table 2. They are divided into the same sub – sectors as in the BAT document. The rank of the listed chemical within the sub sectors can be seen within the parentheses.

Table 2: Capacities of some important organic compounds in Europe based on [UBA GERMANY, 1999]

lower olefins			
compound	capacity	compound	capacity
ethylene (1)	18 700 kt	propylene (2)	12 100 kt
1,3, butadiene (3)	2 282 kt	acetylene (5)	409 kt
aromatics			
compound	capacity	compound	capacity
benzene (1)	8 056 kt	ethyl benzene (2)	4 881 kt
styrene (3)	4 155 kt	toluene (4)	2 635 kt
cumene (5)	2 315 kt	p – xylene (6)	1 342 kt
halogenated compounds			
compound	capacity	compound	capacity
1,2 dichloroethane (1)	10 817 kt	vinyl chloride monomer (2)	6 025 kt
methyl chloride (3)	466 kt	perchloroethylene (4)	434 kt
oxygenated compounds			
compound	capacity	compound	capacity
formaldehyde (1)	6 866 kt	MTBE (2)	3 159 kt
ethylene oxide (4)	1 887 kt	phthalic anhydride (12)	1 008 kt
citric acid (29)	347 kt	maleic anhydride (39)	176 kt
nitrogenated compounds ²⁰			
compound	capacity	compound	capacity
nitrobenzene (1)	1 218 kt	acrylonitrile (2)	1 130 kt
caprolactam (3)	1 095 kt	melamine (9)	270 kt

²⁰ Urea is not included in this list, but has a much higher capacity than nitrobenzene

1.4 Importance of the Chemical Industry in Austria

The chemical industry is one of the largest industrial branches in Austria. Approximately 450 companies with 41 900 employees produce products to the value of more than 100 billions ATS/a. The development of the production from 1989 to 1999 is presented in Table 3.

Table 3: Production of the Austrian chemical industry [WK, 1999]

year	production
1989	92 457 million ATS
1990	91 042 million ATS
1991	90 121 million ATS
1992	88 584 million ATS
1993	84 008 million ATS
1994	87 515 million ATS
1995	92 726 million ATS
1996	94 057 million ATS
1997	100 331 million ATS
1998	104 245 million ATS
1999	107 008 million ATS

The total production of the Austrian chemical industry can be divided into the two major groups chemical products and rubber and synthetic (plastic) products. The development of these two sectors and some sub-sectors can be seen in Table 4.

Table 4: Production of the Austrian Chemical Industry, divided into two branches [ÖSTAT, 1999]

	1997	1998	change
chemical products	55 797.0 million ATS	56 925.7 million ATS	+ 2.0 %
chemical base materials	25 341.1 million ATS	25 022.8 million ATS	- 1.3 %
industrial gases	918.2 million ATS	1 155.6 million ATS	+ 25.9 %
other inorganic base materials and chemicals	1 651.2 million ATS	1 798.5 million ATS	+ 8.9 %
other organic base materials and chemicals	6 269.3 million ATS	6 015.1 million ATS	- 3.9 %
fertilizer and nitrogen compounds ²¹	2 699 million ATS	2 520 million ATS	- 6.6 %
polymers in primary forms	12 337.2 million ATS	11 758.9 million ATS	- 4.7 %
pesticide and plant protective ²¹	876 million ATS	780 million ATS	- 11.0 %
lacquers and paints, printing ink and putty	5 399.2 million ATS	5 645.7 million ATS	+ 4.6 %
pharmaceutics	13 453.3 million ATS	14 025.6 million ATS	+ 4.3 %
soaps, washing agents, cleaning material and personal hygiene materials	2 739.5 million ATS	2 582.5 million ATS	- 5.7 %

²¹ Data are from [WKÖ, 2000] not from [ÖSTAT, 1999]

	1997	1998	change
other chemical products	3 170.9 million ATS	3 271.0 million ATS	+ 3.2 %
man made fiber ²¹	4 069 million ATS	4 356 million ATS	+ 7.1 %
rubber and synthetic products	38 030.5 million ATS	40 542.4 million ATS	+ 6.6 %
rubber products	6 183.3 million ATS	7 363.7 million ATS	+ 19.1 %
synthetic products	31 847.2 million ATS	33 178.7 million ATS	+ 4.2 %
total	93 827.5 million ATS	97 468.1 million ATS	+ 3.9 %

All data from [ÖSTAT, 1999] are given as the total technical production of the respective year. The data from [WKÖ, 2000] are given as sold production during the respective year.

From these data it can be seen that the overall production increased slightly over the last years. The development of the sectors and sub-sectors is quite different. Organic base materials and chemicals decreased from 6 269.3 million ATS in 1997 to 6 015.1 million ATS in 1998, corresponding to a decreasing rate of 3.9 % between 1997 and 1998. In comparison inorganic base materials and chemicals increased from 1997 to 1998 by 8.9 %.

Companies producing large volume organic chemicals that are within the scope of the BRef (see also Figure 1) have been contacted by the Federal Environment Agency to support this study. Questionnaires prepared by the Federal Environment Agency have been sent to the relevant companies. For further information several plants have been visited. The relevant chemicals produced in Austria are presented in Table 5. The capacity or annual production of the Austrian plants is, as far as available, compared with the total production capacities in Europe.

Table 5: Production of Large Volume Organic Chemicals in Austria

	capacity in Austria	capacity in the EC	number of installations in Austrian
ethylene	~ 345 kt	18 700 kt	1
propylene	~ 200 kt	12 100 kt	1
1,3 butadiene	~ 48 kt	2 282 kt	1
acetylene	< 2 kt	409 kt	6
formaldehyde	91 kt	6 866 kt	1
MTBE	67 kt	3 159 kt	1
phthalic anhydride	50 kt	1 008 kt	1
maleic anhydride	~ 26 kt	176 kt	2 at the same site
glyoxylic acid	~ 15 kt		3 at the same site
urea	400 kt ²²	~ 6 000 kt	1
melamine	50 kt (80 kt) ²³	270 kt	3 (4) ²³ at the same site

²² annual production

²³ a new plant will go in operation during 2000

2 LOWER OLEFINS

2.1 Ethylene and Propylene

Nearly the whole amount of ethylene and propylene of the world are produced in steam crackers. In these steam crackers ethylene and propylene are produced with high purity. By – products of ethylene and propylene production are hydrocarbons with four and more carbon atoms. Due to the high purity ethylene and propylene can be used for polymerisation. Input materials for steam crackers may be ethane, propane, butane, naphtha, gas oil and higher boiling distillates. Most of the steam crackers in Europe use naphtha as raw material. Figure 2 presents the distribution of different feedstocks for the ethylene production in Western Europe.

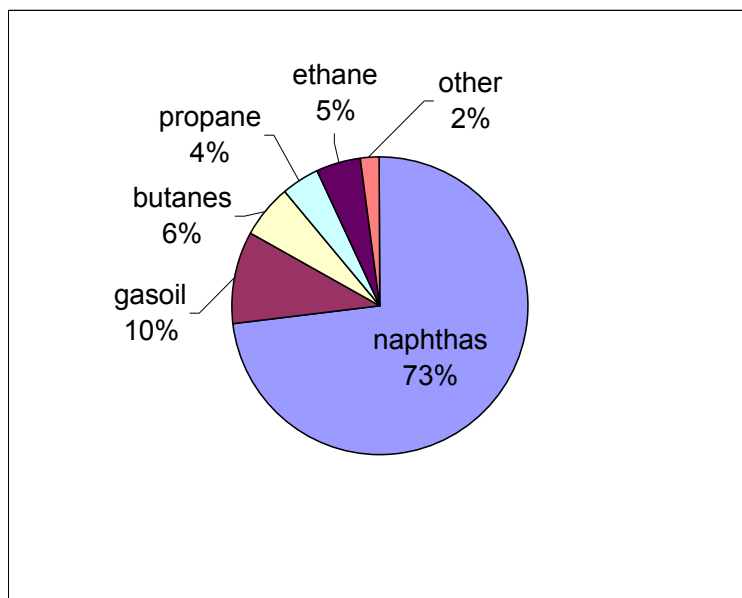


Figure 2: Feedstock for ethylene production in Western Europe [www.cefic.be, 1999]

The development of ethylene and propylene production and production capacity for Western Europe (excluding Greece and Switzerland) from 1993 to 1997 is presented in Figure 3.

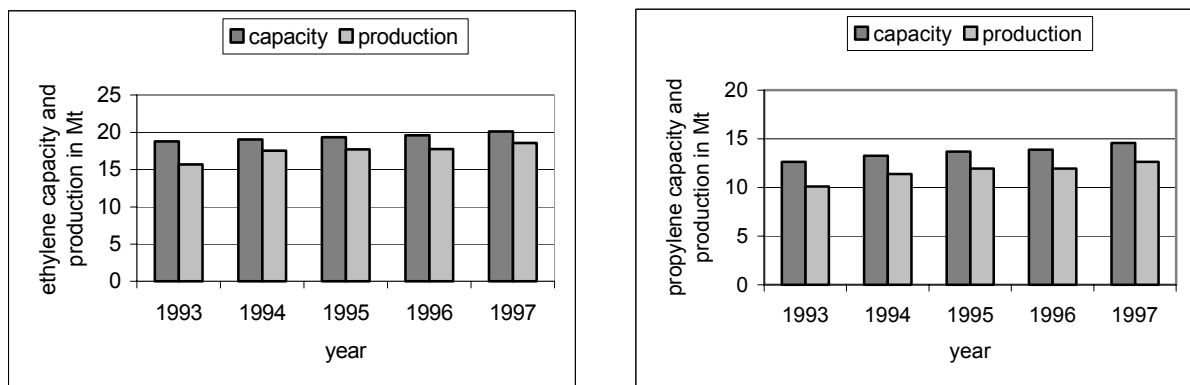


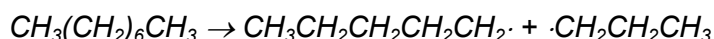
Figure 3: Development of ethylene and propylene production and capacity from 1993 to 1997 [www.cefic.be, 1999]

2.1.1 Ethylene and Propylene Production

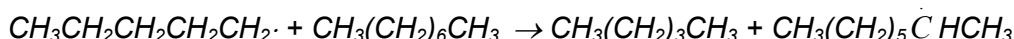
A plant for the production of ethylene and propylene could be divided into three major parts:

- cracking furnace;
- quenching system;
- conditioning processes, including crack gas compression and distillation columns for product separation and purification.

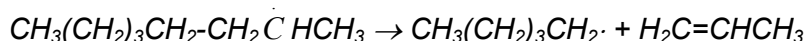
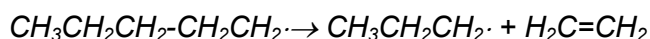
First of all the input materials are mixed with steam. The steam lowers the partial pressure of the hydrocarbons and prevents the formation of coke and tar in the furnace. The mixture of raw material and steam is heated up to temperatures between 800 °C and 900 °C in the cracking furnaces. There they are cracked into smaller hydrocarbons. In this cracking process a radical cleavage is involved. The basic mechanism of a cracking reaction can be envisaged as follows using n-octane as an example. The homolysis of a C-C linkage initiates the thermal cracking process and forms two radicals, e. g.,



Both alkyl radicals can abstract a hydrogen atom from an octane molecule to produce an octyl radical and a shorter alkane, e.g.,



The abstraction of a hydrogen atom is favored on a secondary hydrogen due to the lower C-H bond energy compared to the bond energy of hydrogen atoms of CH₃ groups. Any of these radicals can also undergo β - cleavage to form ethylene, propylene or a shorter alkyl radical.



Thus cracking reactions involve changes in the hydrogen content as well as changes in the carbon network. Cracking reactions could be divided into primary (dehydrogenation, H₂ transfer, C-chain homolysis, isomerization and cyclization) and secondary reactions (olefin polymerisation, alkylation and condensation of aromatics).

To reach high yields of ethylene and propylene high temperatures and short residence times are necessary. A low partial pressure of the hydrocarbons improves the olefin yield. Due to this steam is added and mixed with the hydrocarbons to lower the partial pressure.

A lot of different furnace types exist:

- Conventional cracking furnaces (temperatures up to 810 °C at maximum);
- Short-time cracking furnaces (temperatures between 810 and 885 °C);
- Ultra short-time cracking furnaces (temperatures between 860 and 885 °C).

The furnaces could be distinguished due to the kind of their firing installations. Normally oil and gas are used as fuels. Using an oil burner the fuel usually is added at the bottom and/or the top of the cracking furnace. Examples for this kind of furnace are furnaces from Foster & Wheeler and from Kellog. The other possibility is that the fuel is fed from the side walls into the furnace. In general gas is used as fuel in these firing installations. Examples are the Lummus furnace and the furnace developed by Stone & Webster. Lurgi and Selas devel-

oped furnaces where fuel is added from the bottom and from the side walls. In the last years these installations gained in importance.

Nowadays especially short time cracking furnaces are used, because of their short residence times between 0.4 and 0.6 seconds.

The ratio between propylene and ethylene in the product strongly depends on the cracking conditions, especially on the cracking end temperature. Higher temperatures lead to a higher amount of ethylene in the product stream. The ethylene yield differs between 19 and 30 % depending on the cracking temperature and on the feed composition.

The next important part is the **quenching system**. The aim of the quenching system is to cool down the cracking gases as quickly as possible to suppress reactions of the formed olefins. Additionally high pressure steam, which is used for the turbo-compressors of the crack gas compression and for the cooling processes, is produced in the quenching system. The amount of coke deposition in the quenching system is very important. Due to the deposition of coke the heat transfer between the cracking gas, which should be cooled down and the steam is decreased. This leads to a lower steam production and energy losses and to higher temperatures of the cracking gas after the quenching system.

The quenching system consists of four different stages:

1. Stage: The cracking gas is cooled down in the transfer line heat exchangers from the cracking temperature (800 – 900 °C) to 350 – 400 °C within 0.1 seconds. The transfer line heat exchangers have to be cleaned periodically, because of coke formation due to the separation of polymers.
2. Stage: The cracking gas which leaves the transfer line heat exchanger is rapidly cooled to 200 °C due to the direct injection of quenching oil. The quenching oil mainly consists of pyrolysis oil and is heated up to 180 °C during the oil quenching. High-boiling components of the cracking gas are condensed during this process.
3. Stage: The oil washing column cools the cracking gas to 110 °C. The bottom product of this column is used for the oil injection in stage two. Surplus bottom product could be used as fuel oil.
4. Stage In the fourth stage the cracking gas is cooled with an air cooler to about 50 °C and finally in a water scrubber cooled down to 20 – 30 °C. Liquid cracked gasoline and cracking gas are reached after this stage.

The optimal utilization of waste heat is important for the economic efficiency of steam cracking plants. Table 6 presents the composition of the products of an 450 000 t/a ethylene plant using full range naphtha as raw material with high and medium severity. These different fractions have to be separated in the following stages. The units, which are used for the separation are described in the following pages.

Table 6: Composition of the products of an 450 000 t/a ethylene plant [WINNACKER et al., 1981a]

	high severity	medium severity
input material	amount	amount
full range naphtha	1 345 000 t/a	1 504 000 t/a
product	amount	amount
H ₂ fraction	41 390 t/a	42 280 t/a
CH ₄ fraction	199 400 t/a	179 200 t/a
C ₂ H ₄	450 000 t/a	450 000 t/a

	high severity	medium severity
C ₃ -fraction	199 300 t/a	262 200 t/a
of that C ₃ H ₆	181 900 t/a	245 600 t/a
C ₄ fraction	107 300 t/a	158 900 t/a
of that 1,3-C ₄ H ₆	63 360 t/a	79 400 t/a
petrol	270 700 t/a	356 800 t/a
of that BTX	197 500 t/a	210 500 t/a
fuel oil	76 000 t/a	54 100 t/a
acid gas	670 t/a	720 t/a

For the separation of the cracking gas after the cracking furnace and the quenching system a lot of different stages are needed:

- cracking gas compression;
- separation of acid gas;
- pre-cooling and drying;
- chilling;
- rectification at deep temperatures and high pressures.

The use of deep freezing technologies is necessary, because the distillation of methane and ethylene is only possible if a reflux of liquid methane at the top of the separation column is possible.

Compression of the cracking gas:

For further separation of the cracking gas, it has to be compressed to a pressure between 32 and 37 bar. This pressure is necessary for the production of a highly concentrated hydrogen fraction. For the compression normally turbo compressors are used. In general a five staged process is used for the compression.

Separation of acid gas:

After the third or fourth stage of gas compression carbon dioxide and hydrogen sulphide, are separated from the cracking gas. The cracking gas contains approximately 0.1 Mol % of CO₂ and hydrogen sulphide before the separation. These compounds disturb the further separation of the cracking gas and lead to impurities in the products if they are not separated from the cracking gas. They are separated in a two staged absorption with for example caustic soda (5 – 15 %) or ethanolamine. About three ppm stay in the cracking gas. The caustic soda reacts with H₂S and forms sodium sulphide (Na₂S) in aquatic solution. Sodium sulphide is toxic for the microorganisms in waste water treatment plants. Therefore it is oxidised in a waste lye oxidising plant before it reaches the waste water treatment plant. A lot of different process designs for these oxidising plants exist. One of these designs is described in detail.

The sulphides are oxidised to sulphates in the reactor. For that the waste lye with sodium sulphide and the oxidising air are introduced at the bottom of the reactor and flow in co-current flow through the reactor, where the sulphides are oxidised to sulphates. Simultaneously with the oxidising air that leaves the reactor hydrocarbons are withdrawn from the lye. After the reactor the wet and hot oxidising air is cooled and components that condense during the cooling of the oxidising air are removed back to the oxidised waste lye. The oxidised waste lye is then neutralised with sulphuric acid. After neutralisation residual hydrocarbons

are stripped with air from the waste lye. The oxidising and stripping air is combusted in the last step and the neutralised lye is further treated in the waste water treatment plant. Table 7 presents the parameters for the oxidation of 4 m³/h lye with a maximum sulphide content of 25 kg/h [WITZLEB & HEISEL, 1997]

Table 7: Parameters of a waste lye oxidation plant [WITZLEB & HEISEL, 1997]

	electric energy	steam 16 bar	cooling water	air 7 bar	sulphuric acid	heating gas
amount	20 kW	340 kg/h	27 m ³ /h	480 kg/h	90 kg/h	24 m ³ /h

Pre-cooling and drying:

The gas from the last compression stage is now cooled down in several stages. After pre-cooling the water is separated from the gas with molecular sieves, that the subsequent low temperature distillation will not be interrupted by ice formation. The remaining content of water is approximately 2 mg/m³. For further cooling cold products from the low temperature separation are used. Evaporated propylene is used for the cooling process, too.

Separation of the C₃ fraction and of higher hydrocarbons (C₂/C₃ Splitter):

In this column the gas is separated in two fractions at a pressure of 35 bar. At the top of the column the C₂ fraction and lower hydrocarbons are discharged and further treated in the low temperature part. The bottom product consists of the C₃ fraction and higher components. This fraction is further treated at temperatures higher than the dew point of water.

Deep freezing and production of C₂ hydrocarbons:

Normally the top product of the previous described column is selectively hydrogenated at Pd catalyst to remove acetylene, because acetylene interferes with the polymerisation of ethylene. Another possibility for the separation of acetylene is extractive distillation, e.g. with dimethylformamide or N-methylpyrrolidone.

The hydrogenated raw gas is cooled down step by step with evaporating ethylene and the C₂ mixture from the bottom of the methane column. During this ethylene, ethane and the main part of methane condense. The remaining gas has a hydrogen content of about 85 Mol %. The condensates which are rich in ethylene are fed into the C₁/C₂ separation column. At the top of the column normally methane is recovered with a purity of 95 %. The bottom product is the C₂ fraction mainly containing ethane and ethylene. This fraction is fed to the ethylene/ethane column for further separation.

Ethylene/ethane separation (C₂ Splitter):

The ethylene column works at a pressure of approximately 9 bar. Ethylene is enriched in the top product up to a purity of 99.9 %. The bottom product ethane is recirculated to the cracking oven after a heat recovery in the pre-cooling stage. The recirculation of ethane increases the yield of ethylene. Ethylene with such high purity could be used as raw material in the chemical industry (e. g. for the production of polyethylene).

C₃/C₄ separation (C₃/C₄ Splitter):

As mentioned before the bottom product of the first separation step is further separated. In the first following column this fraction is separated into a C₃ fraction and a so called C₄ frac-

tion. At the top of this column the C₃ fraction including propylene, propane, propadiene and propine is enriched and discharged. The bottom product contains the C₄ fraction and the higher hydrocarbons. The further separation of the C₃ fraction is described later.

C₄/C₅ separation (C₄/C₅ Splitter):

The bottom product of the previous column is fed into the next column. There the C₄ fraction and the pyrolysis petrol are separated. The column works at a pressure of 6 bar and is cooled with water. The bottom product (pyrolysis petrol) could be mixed with the liquid cracking fuel from the fourth step of the quenching system. This mixture is treated in a petrol hydrogenation unit and could be used as a component with high octane number for the addition to fuels or for the production of aromatics. The C₄ fraction (top product) is separated in several following steps described in Chapter 2.2.

Separation of the C₃ fraction:

The following Table presents the composition of a typical C₃ fraction from steam crackers.

Table 8: Composition of a typical C₃ fraction of a steam cracker [WINNACKER et al., 1981b]

component	amount
propylene	91 – 94 Vol. %
propane	3 – 6 Vol. %
propadiene and propine	1 – 4 Vol. %

The C₃ fraction could be separated in two different qualities of propylene:

1. **Chemical grade:** For this quality propadiene and propine are selectively hydrogenated, because these compounds disturb in further utilizations. The product contains between 92 and 94 % propylene and should contain less than 20 ppm propine and propadiene in sum after the selective hydrogenation.
2. **Polymerisation grade:** For polymerisation propylene of high purity is necessary. The content should be between 99 and 99.9 %. The main problem is the separation of propane, because the boiling points of propane and propylene are quite similar. Possible processes are rectification and extractive distillation. Before propane is separated the C₃H₄ compounds (propine and propadiene) are again hydrogenated.

An overview of the above described separation processes of the product gases is given in Figure 4.

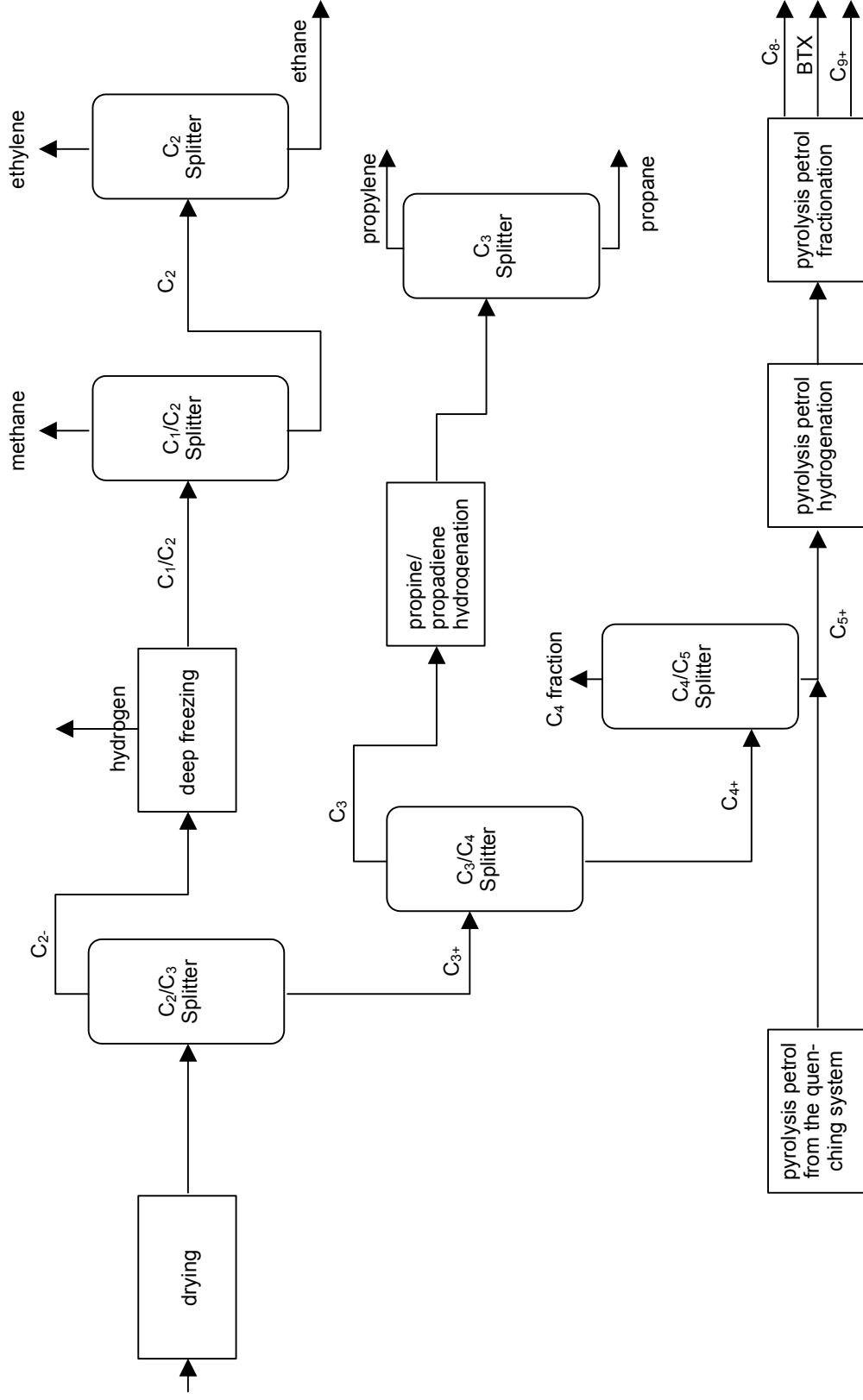


Figure 4: Separation of the product gases of a steam cracker

2.1.2 Energy and Emissions

The steam cracking is one of the most energy intensive processes in a refinery. In nowadays operated steam crackers approximately 0.5 m³/t_{ethylene} process waste water is produced. This leads to the formation of 22 m³/h in a steam cracker with a capacity of 350 000 t/a [KRAUSE & PETZNY, 1993]. The emission of hydrocarbons for different plants with an input of 1.8 million tonnes naphtha per year was 0.3 t/d in 1987 [KRAUSE & PETZNY, 1993]. Table 9 presents the atmospheric emissions and the waterborne emissions from the production of ethylene in Europe starting with the crude oil production or the natural gas production. The results of two different studies, both made by industry are compared in this Table.

Table 9: Total atmospheric and waterborne emissions for the production of ethylene in Europe (kg/1000 kg Ethylene) [FRANKE et al., 1995]

	APME study	CEFIC study
air emissions		
dust	1 kg/t _{Ethylene}	1.78 kg/t _{Ethylene}
carbon monoxide	0.6 kg/t _{Ethylene}	0.5 kg/t _{Ethylene}
carbon dioxide	529 kg/t _{Ethylene}	1257 kg/t _{Ethylene}
sulphur oxides	4 kg/t _{Ethylene}	4.12 kg/t _{Ethylene}
nitrogen oxides	6 kg/t _{Ethylene}	10.9 kg/t _{Ethylene}
hydrogen sulphide	0.01 kg/t _{Ethylene}	0 kg/t _{Ethylene}
hydrogen chloride	0.02 kg/t _{Ethylene}	0.026 kg/t _{Ethylene}
hydrocarbons	7 kg/t _{Ethylene}	16.7 kg/t _{Ethylene}
other organics	0.001 kg/t _{Ethylene}	0.018 kg/t _{Ethylene}
metals	0.001 kg/t _{Ethylene}	0.0016 kg/t _{Ethylene}
water emissions		
COD	0.2 kg/t _{Ethylene}	0.13 kg/t _{Ethylene}
BOD	0.04 kg/t _{Ethylene}	0.037 kg/t _{Ethylene}
acid as H ⁺	0.06 kg/t _{Ethylene}	0.039 kg/t _{Ethylene}
metals	0.3 kg/t _{Ethylene}	0.23 kg/t _{Ethylene}
chloride ions	0.05 kg/t _{Ethylene}	0 kg/t _{Ethylene}
dissolved organics	0.02 kg/t _{Ethylene}	0 kg/t _{Ethylene}
suspended solids	0.2 kg/t _{Ethylene}	0.12 kg/t _{Ethylene}
oil	0.2 kg/t _{Ethylene}	0.004 kg/t _{Ethylene}
phenol	0.001 kg/t _{Ethylene}	0.002 kg/t _{Ethylene}
dissolved solids	0.5 kg/t _{Ethylene}	0.46 kg/t _{Ethylene}
other nitrogen	0.01 kg/t _{Ethylene}	0 kg/t _{Ethylene}
solid waste	12.4 kg/t _{Ethylene}	16.02 kg/t _{Ethylene}

During the cracking of hydrocarbons small amounts of oxygen containing hydrocarbons are produced. The most important are methanol (ca. 10 ppm), acetaldehyde (ca. 15 ppm), a few ppm acetone and acetic acid. Part of the methanol leaves the plant with the waste water and increases the COD and BOD value in the biological waste water treatment. Aldehydes pol-

lute the C₄ fraction and may cause problems in the acid gas separation if only a caustic scrubber is used due to the formation of layings due to aldol condensation. Most of the organic acids are condensed with process steam in the water scrubber. For neutralization chemicals are needed and further more they pollute the waste water [BAUR, 1997].

2.1.3 Start up of ethylene plants

During the start up of ethylene plants generally a lot of gas is produced, which is combusted in the flare system. The start up times of ethylene plants differ between 15 hours up to a few days. During this time the products of the cracking furnaces have to be incinerated in the flare system. Up to 60 tonnes flare gas are produced per hour during the start up. This results in a total emission of up to 1000 tonnes and more during the whole start up time. A start up technology without using the flare system was developed by the LINDE AG [BAIRLEIN et al., 1997]. As early as 1982 this concept was developed and started with the first industrial application in Portugal. The advantages of the flareless start up are a huge reduction of the exhaust gas and a reduction of noise pollution. Further the product losses due to the start up operation are minimised. Therefore the minimisation of start up losses is also interesting for economic reasons not only for ecological reasons.

2.1.4 Use of Lower Olefins

- a) **Ethylene:** Ethylene is one of the most important raw materials in the organic chemistry. It is used for the production of polyethylene, ethylene oxide and ethylene glycol, vinyl chloride, styrene and a lot of other applications. The most important products are presented in Figure 5.

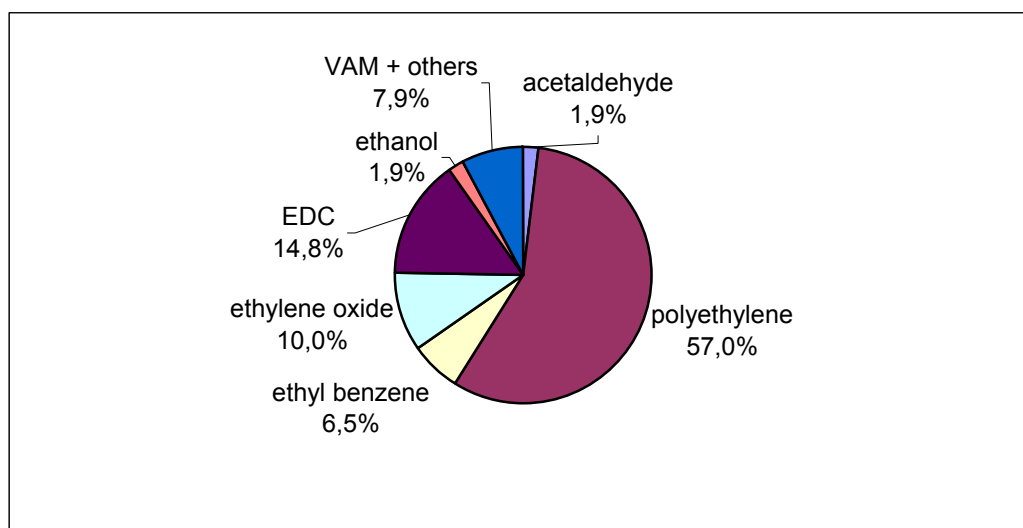


Figure 5: Use of the produced ethylene in Western Europe [www.cefic.be, 1999]

- b) **Propylene:** The other main product of steam crackers is propylene and is also an important raw material in the organic chemistry. Examples for the use of propylene are the production of polypropylene, acrylonitrile, isopropanol, propylene oxide or cumene.

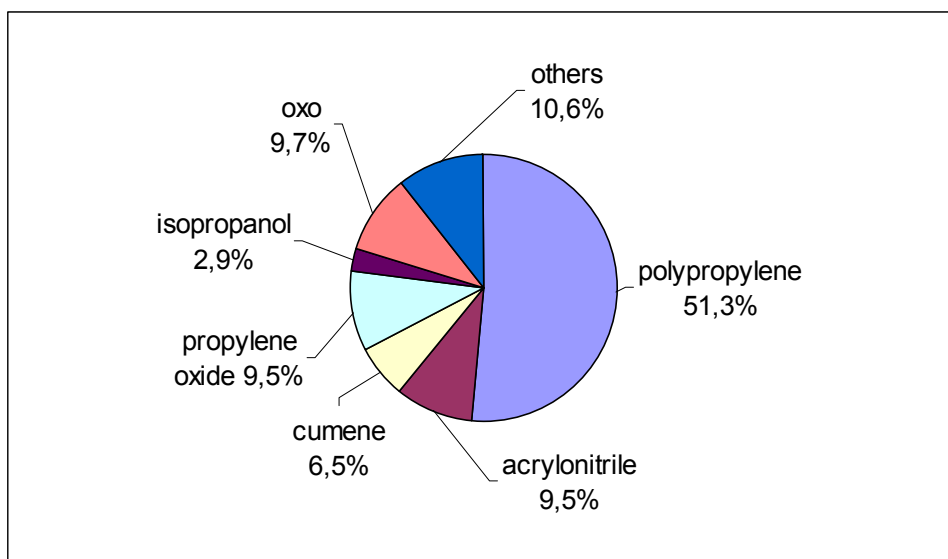


Figure 6: Use of the produced propylene in Western Europe [www.cefic.be, 1999]

2.1.5 Austria

In Austria one steam cracker works in the refinery of the OMV – AG at Schwechat. Its capacity is 345 000 tonnes ethylene per year, with an input of approximately 1 100 000 t/a naphtha, LPG²⁴ and ethane. Table 10 shows the yields of the different products in the Austrian steam cracker. The yields can vary a little bit depending on the composition of the input materials.

Table 10: Yields of the products during steam cracking

product	yield
ethylene	25 – 30 %
propylene	15 – 20 %
C ₄ fraction	approx. 10 %
pyrolysis petrol	approx. 25 %
gas and oil	approx. 20 %

Ethylene and propylene are produced in high purity, thus they can be used for polymerisation. Approximately 40 % of the C₄ fraction is butadiene, which is extracted in a further separation step (see Chapter 2.2). The rest of the C₄ – fraction is either used for MTBE production (isobutene) or is added to petrol.

The Austrian plant has six cracking furnaces for naphtha, one for liquefied petroleum gas and one for ethane. For the energy supply of these cracking furnaces refinery gas is combusted. The thermal output of these furnaces is approximately 298 MW_{th}. The fuel refinery gas is a mixture of residual gases of the production processes in a refinery, which contains hydrogen, hydrocarbons (up to five C – atoms), nitrogen and hydrogen sulphide. In general

²⁴ LPG...liquefied petroleum gas

this gas is characterised by the hydrogen sulphide amount and the net calorific value. The emissions of the cracking furnaces in 1997 and the emission limits for these furnaces are presented in Table 11. Data are from the Dampfkesseldatenbank of the Federal Environment Agency of Austria.

Table 11: Emissions of the cracking furnace

	dust	SO ₂	NO ₂	CO
amount	2.309 t/a	3.356 t/a	378.048 t/a	23.763 t/a
concentration	–	–	116 – 206 mg/m ³	< 8 – 26 mg/Nm ³
emission limit	10 mg/m ³	–	200 mg/m ³	100 mg/m ³

For the separation of the acid gas a scrubbing column is used. As washing solution caustic soda is used. After the scrubbing column the loaded waste lye is oxidized in a waste lye oxidation plant to sodium sulphite and sodium sulphate.

After the separation of the acid gas the cracking gases are dried and subsequently separated into the different fractions as described in Chapter 2.1.1. Additionally it has to be mentioned that methane, hydrogen and carbon monoxide, which are removed together, are fed to a methanation reactor. There CO, which destroys the catalysts in hydrogenation reactors, is converted to methane. The CO free hydrogen is used for the hydrogenation of the C₃ fraction and the pyrolysis gasoline. Separated ethane is recirculated to the cracking furnace to increase the yield of ethylene.

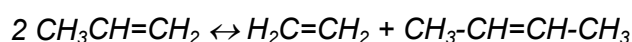
The following Table presents energy consumption, throughput and total emissions of this steam cracker in the year 1997.

Table 12: Emissions from the steam cracker in Schwechat (year mean value, related to 3 % O₂) [UBA, 2000]

	energy consumption [GWh/a]	throughput [t/a]						dust
			SO ₂	NO _x	CO	CO ₂		
steam cracker	2 323.2	1 100 000 naphtha	[mg/m ³]	1	164	10	-	1
			[t/a]	2.3	377	23	450 692	2.3
			[kg/t Input]	0.002	0.343	0.021	410	0.002

2.1.6 Metathesis of Olefins

The olefin metathesis is one process that could be used if the need of propylene increases quicker than the need of ethylene. The metathesis is an exchange reaction between two olefins in which alkylidene groups are interchanged. The simplest example for a metathesis reaction is the reaction of two mols propene to form one mol ethylene and one mol butene (mainly 2-butene).



Due to the transition of an olefin with a certain carbon number in two other olefins of lower and higher carbon number this kind of reactions is called disproportionation of olefins (or metathesis). The catalyst system for the metathesis reactions are generally based on molybdenum, tungsten or rhenium.

With the metathesis process the amounts of the different products of steam cracking can be adapted to the needed ratio.

The Austrian refinery in Schwechat does not use the metathesis process.

2.2 Separation of the C₄ Fraction

The C₄ fraction of the steam cracker can consist of twelve different compounds with four carbon atoms. This mixture is very difficult to separate. It is impossible to separate this mixture with normal distillation, because the boiling points of the different components are close together and some of the components for example butane and butadiene form azeotropes.

The first step in the separation of the C₄ fraction is the butadiene extraction. In most cases afterwards a selective butadiene hydrogenation follows to eliminate the rest of the butadiene. The third step is the separation of the remaining butene fraction.

2.2.1 Butadiene Extraction Processes

The extractive distillation is a process that is very well suitable for the work up of butadiene from C₄ fractions. The other possibility, liquid-liquid extraction is not in use in Europe. The content of butadiene in the cracking gas of a steam cracker strongly depends on the feedstock of the steam cracker. The following Table summarises the amounts of butadiene related to one tonne ethylene at different feedstocks in a steam cracker.

Table 13: Butadiene content in kg/t_{ethylene} using several feedstocks [WEISSERMEL & ARPE, 1998a]

feedstock	butadiene
ethane	10 – 20 kg/t
propane	40 – 70 kg/t
n-butane	70 – 110 kg/t
naphtha	120 – 150 kg/t
gas oil	180 – 240 kg/t

Due to the addition of selective solvents to the C₄ fraction the volatility of butadiene is lowered and additionally the highly unsaturated hydrocarbon is also more soluble in the polar solvent. The highly unsaturated hydrocarbons remain in the solvent at the bottom of the column, while the impurities (e. g. butene and butane), previously inseparable by distillation, can be removed overhead. Table 14 shows an overview of established processes using different solvents.

Table 14: Different processes for extractive butadiene distillation [WINNACKER et al., 1981]

licensor	solvent
BASF	N-methylpyrrolidone
Nippon Zeon	dimethylformamide
Shell, UOP or Atl. Richfield	acetonitrile
Monsanto	Methoxypropionitril

licensor	solvent
Phillips	furfurol
Union Carbide	dimethylacetamide

An example for one of these processes, which is used in the Austrian plant is described in Chapter 2.2.3.

2.2.2 Production and Use of Butadiene

In Figure 7 the development of butadiene production and production capacity in Western Europe (excluding Greece and Switzerland) from 1993 to 1997 is presented.

The main part of the produced butadiene is used for the production of synthetic rubbers and polymers. The most important rubbers and polymers are: styrene/butadiene rubber; polybutadiene rubber; styrene/butadiene latex.

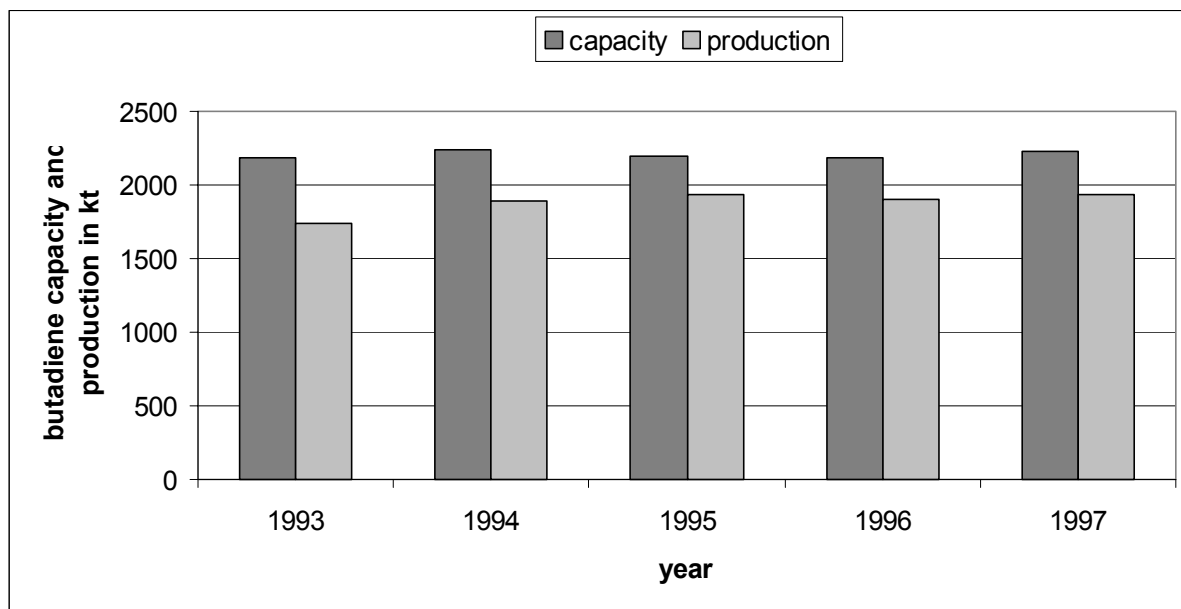


Figure 7: Development of butadiene production and production capacity in Western Europe [www.cefic.be, 1999]

2.2.3 Butadiene Production in Austria

The capacity of the Austrian plant is 48 000 tonnes per year. The yearly production is between 40 000 and 45 000 tonnes.

The solvent used in Austria is N-methylpyrrolidone (NMP). As mentioned in Chapter 2.2.1 the extractive distillation process with NMP is described here.

The C₄ fraction is added to the washing column at the bottom, while the solvent (NMP) is added at the top of the column. The saturated and less unsaturated hydrocarbons leave the column at the top, whereas the more unsaturated hydrocarbons like acetylenes, butadiene and C₅ hydrocarbons are discharged with the solvent at the bottom.

This bottom product is fed to the top of the rectifier. In the middle of the rectifier, where butadiene has its highest concentration, a stream containing 1,3 butadiene, 1,2 butadiene, propyne, butyne and the C₅ hydrocarbons is discharged and fed to the bottom of the so called after-washer. The after-washer is again an extractive distillation unit, where NMP is added at the top. The aim of this unit is the separation of the acetylenes, which are solved in NMP in the bottom product of this column and removed to the rectifier. The top product consists of 1,3 butadiene, 1,2 butadiene, propyne and a C₅ fraction.

This top product is further separated in two distillation columns. In the first column propyne is separated from the product stream. The more volatile propyne is removed from the top of this column while the rest (bottom product) is fed to the second distillation column. There 1,3 butadiene is finally separated from 1,2 butadiene and the C₅ fraction.

The bottom product of the rectifier containing the solvent and acetylenes is led into the degassing tower. There the solvent (NMP) and the acetylenes are separated. NMP is recirculated to the process. For the treatment of the acetylene fraction different possibilities exist.

First the acetylene stream is washed in an acetylene washer and then possibly discharged from the process or fed to a selective hydrogenation reactor and then after hydrogenation re-fed to the first washing column.

2.2.4 Separation of the Butene Fraction

After the separation of butadiene the remaining C₄ fraction will contain especially isobutene, n-butenes and butanes. A detailed description of the compositions of this C₄ fraction can be seen in the following Table. This remaining mixture is called C₄ raffinate.

Table 15: Typical composition of a C₄ raffinate [WEISSERMEL & ARPE, 1998b]

component	concentration
isobutene	44 – 49 Vol. %
1-butene	24 – 28 Vol. %
2-butene	19 – 21 Vol. %
n-butane	6 – 8 Vol. %
isobutane	2 – 3 Vol. %

A separation with extractive distillation is impossible for this mixture, because the boiling points of the different compounds are too close together and the selectivity of different solvents is too low. The main processes for the separation use the reactivity of isobutene (especially hydration reactions in the presence of acids) or the absorption of n-butene on molecular sieves.

The most reactive compound in the C₄ raffinate is isobutene. This property is used for chemical separation of isobutene. Four different processes have been successfully commercialised, but only two can be used as reversible processes. One of these processes uses the addition of water to isobutene and the other uses the addition of alcohols (especially methanol) to isobutene. In the second process MTBE is formed. This process is described later in a separate Chapter about MTBE production (see Chapter 4.3).

Hydration of isobutene:

In the commercial hydration of isobutene in general 50 – 60 % H₂SO₄ is used. Isobutene is removed from the C₄ raffinate in a countercurrent extraction at 10 – 220 °C as tertiary butanol. After the dilution of the acidic solution with water tertiary butanol is separated from the solution with vacuum distillation. Then tertiary butanol can be used as intermediate or for the regeneration of isobutene. For the regeneration a catalytic dehydration process is used. Afterwards the raw isobutene is cleaned in a rectification column.

2.2.5 Use of the different Parts of the C₄ Fraction

The different possibilities for the use of components of the C₄ fraction of a steam cracker are presented in Figure 8. Only the main components of the C₄ fraction (butadiene, isobutene and n-butene) are included in this Figure. Additionally to the presented possibilities for the use of C₄ fraction after the separation, it should be mentioned the parts of the C₄ fraction, which are not separated can be used as a blending component for gasoline production.

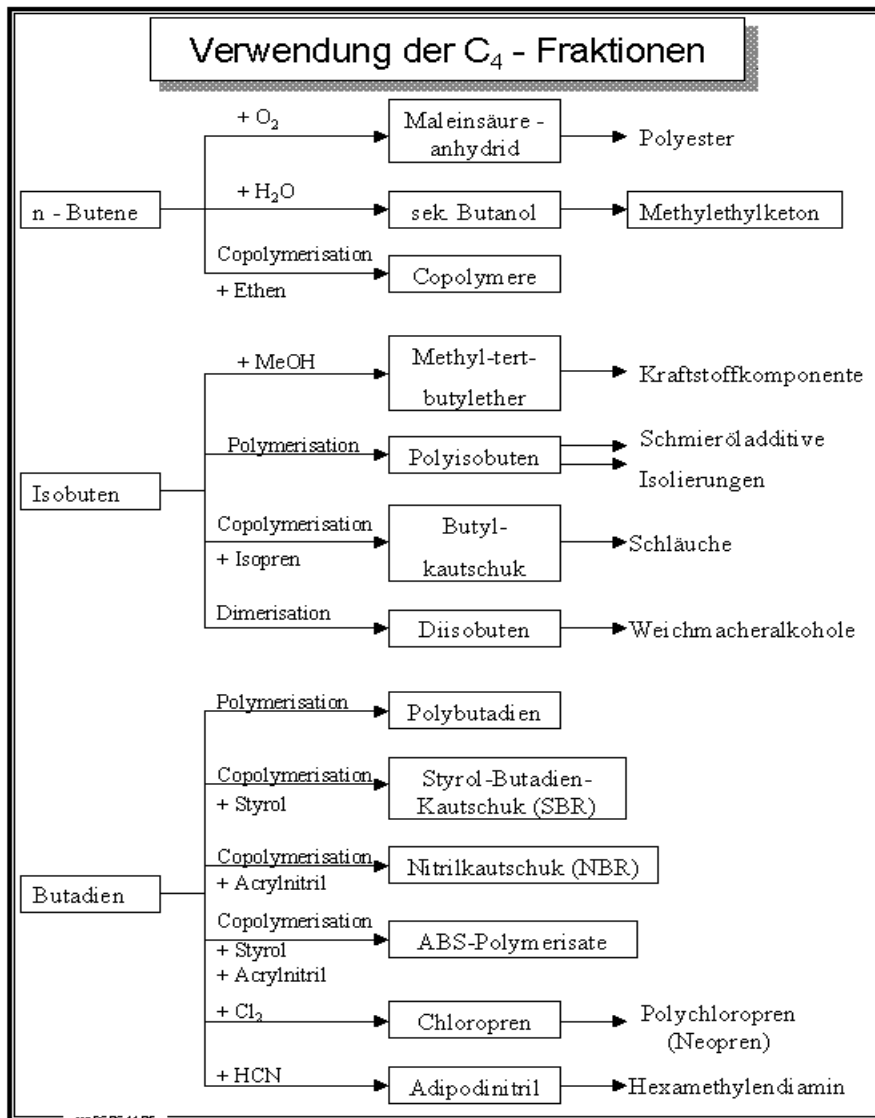


Figure 8: Use of the C₄ fraction [fb9-tc2.chemie.uni-oldenburg.de, 1999]

2.2.6 Austria

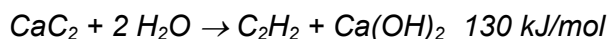
As described above butadiene is extracted from the C₄ fraction using extractive distillation with NMP. The remaining isobutene is used for the production of MTBE. The capacity of the MTBE plant is 67 000 tonnes per year. The remaining C₄ fraction (Raffinate 2) after MTBE production is no more separated and used as blending component for gasoline production or as feedstock for the steam cracker.

2.3 Acetylene

The production processes of acetylene can be divided into two completely different groups. One part of the processes uses calcium carbide as raw material, whereas different thermal processes manufacture acetylene by pyrolysis of different hydrocarbons.

2.3.1 Production based on Calcium Carbide

Acetylene is produced from calcium carbide in an exothermic reaction with water. A by-product of this reaction is lime hydrate.



The reaction heat of 130 kJ/mol is removed by cooling with the added water or evaporation of a portion of the added water. Due to the amount of water which is added, dry generation processes and wet generation processes can be distinguished.

The **wet generation process** works with high water excess to remove the reaction heat. A lime sludge with 10 – 20 % water content is produced.

The **dry generation process** uses only as much water as necessary to guarantee a maximum temperature of 110 °C for acetylene at the outlet of the reactor. The reaction heat is removed as the evaporation heat of the added water. The by – product of this process is pulverized lime hydrate with a water content between 1 – 5 %.

Due to the process pressure low pressure and medium pressure processes can be distinguished. After the production the dry gas contains 99.5 – 99.8 % acetylene. Especially if acetylene is used as a welding gas higher product qualities have to be reached. The main impurities are sulphur containing compounds and hydrogen phosphide. The amount of impurities mainly depends on the content of sulphur and phosphorus in the raw material calcium carbide. Using a dry generation process the sulphide content is between 300 and 400 ppm. The ammonia content is approximately 20 ppm. For wet generation processes the sulphide content is lower between 60 and 70 ppm, whereas the ammonia content is higher with 150 – 200 ppm compared with dry generation processes [WINNACKER et. al., 1981].

For the **purification of the acetylene** different methods exist. Small production units can use so called purifying masses. These purifying masses are porous masses like diatomite or pumice with ferric chloride or chromic acid. The other possibility for larger acetylene plants are three staged scrubbers. The different stages are mentioned below.

- **Stage one:** The first step is the removal of NH₃ with dilute acids e. g. H₂SO₄;
- **Stage two:** In the second stage the raw acetylene is irrigated with 98 % H₂SO₄, hypochlorite solution or chlorine water. Thus the phosphorus and sulphur containing impurities are oxidised and washed out;
- **Stage three:** It is to remove traces of acids from the gas. In general caustic soda solution is used for the last step of acetylene purification.

Wastes and By - Products:

The main by-product of acetylene production from calcium carbide is lime hydrate. Lime hydrate can be utilised in different processes and industrial branches. Examples are :

- the production of cement and mortar;
- the use in the chemical industry for neutralization;
- the use in the agriculture (as fertilizing lime);
- the use in the waste water treatment;
- the use in flue gas cleaning systems of firing installations.

2.3.2 Thermal Processes

Numerous processes for the manufacture of acetylene are based on non-catalytic pyrolysis of hydrocarbons. As feedstocks a big range of hydrocarbons can be used from methane to crude oil. For all different processes the following important requirements are necessary:

- rapid energy transfer;
- high temperature level ($T > 1400\text{ °C}$);
- very short residence times between 0.01 to 0.001 seconds for feed and reaction products;
- low partial pressure of acetylene;
- rapid quenching of the pyrolysis gas.

The acetylene present in the cracked gas is very dilute (5 to 20 Vol. %). For separation from the gas mixture it is extracted with selective solvents like DMF, NMP, kerosene, methanol or acetone. In further steps it is purified.

The individual processes differ mainly in the type of generation and transfer of the high temperature heat, which is required for the pyrolysis reactions. Three different basic principles can be found.

2.3.2.1 Allothermal Processes with direct Heat Transfer²⁵

The most important processes are the arc process and the plasma process.

The mean reaction temperature in the **arc process** is between 1400 and 1500 °C. The residence time is between 2 and 3 ms. The disadvantage of this process is that the temperature distribution in the arc is not homogeneous and thus overheatings can appear. In these zones the produced acetylene could be decomposed to hydrogen and carbon and thus the yield of acetylene will decrease.

The **plasma process** solves this problem by realising the reaction in a hydrogen plasma. In the first step in an arc a hydrogen plasma is produced at temperatures between 3500 and 4000 K. This plasma contains 30 – 65 % hydrogen atoms. In the second step the hydrocarbons are injected into the plasma. The reaction takes place between 1000 – 1700 °C. The residence time is between 1 and 4 ms.

Table 16 presents the amount of raw materials, of energy and the amounts of produced by-products during the production of one tonne acetylene in an arc process.

Table 16: Raw material and energy consumption and by-product production during acetylene production [WINNACKER et al., 1981]

product		by-products	
acetylene	1 000 kg	ethylene	450 kg
raw materials		hydrogen	300 kg
hydrocarbons	2 500 kg	light oil	150 kg
energy consumption		soot	600 kg
electrical energy	9 600 kWh		

²⁵ usually with electrical heat

If methane is used as raw material the energy consumption is rising up to 11 800 kWh per tonne acetylene.

2.3.2.2 Allothermal Processes with indirect Heat Transfer

These processes use heat transfer agents for the heat transfer. For the heat transfer agents different possibilities exist. One process uses fireproof stones, whereas other processes use the exhaust gas of the combustion of a heating gas. The third variant uses super heated steam.

2.3.2.3 Autothermal Processes

The heat is generated due to the combustion of part of the feed. For heating of the raw material in the reactor part of the raw material is combusted. Input materials are methane, liquid gas or light petroleum and oxygen for the partial combustion. The reaction temperature is approximately 1400 °C. In the first step the hydrocarbons and oxygen are heated separately in a pre-heater. In this stage no cracking of the raw material and no spontaneous inflammation should take place. After the reaction, where the raw materials are cracked to acetylene and other products the cracking gas is quenched with water. The reaction heat is removed with the water at a temperature of approximately 80 °C. The composition of the cracking gas strongly depends on the cracking temperature and thus on the ratio between hydrocarbons and oxygen.

2.3.3 Use of Acetylene

The importance of acetylene as a basic raw material for a lot of products decreased since processes using ethylene, propylene or butadiene were developed. Nowadays applications of acetylene are the production of butanediol and the use as a welding gas.

2.3.4 Austria

In Austria three different companies produce acetylene at six different plants. All six plants use calcium carbide as raw material and a wet generation technology for acetylene production. For the purification of acetylene a two or three staged scrubber system is used, using H₂SO₄ and caustic soda solutions in the scrubbers. In all cases the regeneration of the washing liquid is made by the supplier.

The produced lime sludge is used in different applications. One company uses its lime sludge in clarification plants or as a fertilizer, whereas an other company sells its sludge for the use in the flue gas cleaning systems of an electric power plants. Also the use for neutralization of waste water is one possibility. According to information of the companies no waste water is produced, because the scrubbing water is recirculated in all plants. The reaction heat is not recovered in any plants.

The total production of five of the six Austrian plants in 1998 was 1 497 tonnes.

Table 17 presents data about the acetylene production in three of the six different plants in Austria for 1998.

Table 17 *Input and output data from acetylene production [Evaluation of returned questionnaires of three Austrian companies]*

plant 1	plant 2	plant 3
---------	---------	---------

	plant 1	plant 2	plant 3
capacity			
acetylene		350 kg/h	120 kg/h
input			
calcium carbide	702.9 t/a	480 t/a	700 t/a
output			
acetylene	327 t/a	160 t/a	280 t/a
lime sludge	2 312.4 t/a		
residues			
H ₂ SO ₄	11 390 kg/a	7 600 kg/a	Σ washing solutions: 12 000 kg/a
NaOH	9 490 kg/a	6 250 kg/a	

3 BTX PRODUCTION²⁶

For commercial isolation of aromatics three different sources of feedstocks are available:

- Coke oven gas from coking of hard coal;
- Reformate gasoline from processing of crude gasoline;
- Pyrolysis gasoline from steam crackers.

Table 18 presents the different sources for BTX production in Western Europe, Japan and USA in the year 1986, 1990 and 1994.

Table 18: Raw material sources for BTX production in % [WEISSERMEL & ARPE, 1998a]

	OIL			COAL		
	1986	1990	1994	1986	1990	1994
USA	97 %	98 %	99 %	3 %	2 %	1 %
Western Europe	96 %	95 %	96 %	4 %	5 %	4 %
Japan	90 %	93 %	98 %	10 %	7 %	2 %

The column of oil consists of two different raw materials. One is reformate gasoline which is formed in different reforming units in a refinery and the other raw material is pyrolysis gasoline which results from steam cracking of naphtha for the production of ethylene, propene and higher olefins. In Table 19 the development of production capacity and production of the BTX fraction in Western Europe (excluding Switzerland and Greece) is presented. Additionally production capacity and production of other important aromatics are shown.

Table 19: Capacity and production of aromatics [MWW.CEFIC.BE, 1999]

		1993	1995	1997
Benzene	Capacity	7 308 000 t	7 502 000 t	7 359 000 t
	Production	5 512 000 t	6 503 000 t	6 505 000 t
Toluene	Capacity	2 538 000 t	2 669 000 t	2 657 000 t
	Production	1 900 000 t	2 189 000 t	2 163 000 t
Paraxylene	Capacity	1 217 000 t	1 349 000 t	1 429 000 t
	Production	1 101 000 t	1 292 000 t	1 303 000 t
Orthoxylene	Capacity	656 000 t	695 000 t	714 000 t
	Production	559 000 t	585 000 t	611 000 t
Nitrobenzene	Capacity	993 000 t	1 063 000 t	1 304 000 t
	Production	649 000 t	912 000 t	1 070 000 t
Cyclohexane	Capacity	1 060 000 t	1 147 000 t	1 110 000 t
	Production	763 000 t	1 006 000 t	958 000 t
Phthalic Anhydride	Capacity	945 000 t	836 000 t	876 000 t
	Production	754 000 t	685 000 t	780 000 t
Aniline	Capacity	695 000 t	752 000 t	872 000 t
	Production	482 000 t	684 000 t	801 000 t
Maleic Anhydride	Capacity	209 000 t	252 000 t	235 000 t
	Production	174 000 t	190 000 t	205 000 t

²⁶ BTX...Benzene, Toluene, Xylene

While reformat gasoline can be used directly for the production of aromatics, pyrolysis gasoline must be freed from polymerizable mono- and diolefins by hydrogenation. Usually the hydrogenation is done in two stages. Nitrogen, sulphur and oxygen containing compounds are also removed during the hydrogenation. A typical commercial process uses Pd and Ni-W catalysts (e. g. IFP²⁷ process), whereas other processes use CoO-MoO₃/Al₂O₃ catalysts at 300 – 400 °C and 20 – 40 bar.

A simplified picture of the compositions of reformat gasoline and pyrolysis gasoline neglecting the influence of different reforming and cracking conditions is presented in Table 20.

Table 20: Typical compositions of reformat and pyrolysis gasoline in % [WEISSERMEL & ARPE, 1998b]

product	reformat gasoline	pyrolysis gasoline
Benzene	3 %	40 %
Toluene	13 %	20 %
Xylenes	18 %	4 – 5 %
Ethylbenzene	5 %	2 – 3 %
Higher aromatics	16 %	3 %
Non-aromatics	45 %	28 – 31 %

3.1 Isolation of BTX

The isolation of aromatics consists of stages for the separation of the non-aromatics, followed by the separation of the aromatics. Both of these separations are very difficult, because some of the components form azeotropes or the differences in the boiling points of some components are very small. Thus some very special separation processes have been developed to solve these problems.

Table 21: Processes for the aromatics recovery [WEISSERMEL & ARPE, 1998c]

Process	Separation problem	Requirements for basic or economical operation
Azeotropic distillation	BTX separation from pyrolysis gasoline	High aromatic content (> 90 %)
Extractive distillation	BTX separation from pyrolysis gasoline	Medium aromatic content (65 - 90 %)
Liquid-liquid extraction	BTX separation from reformat gasoline	Lower aromatic content (20 - 65 %)
Crystallisation by freezing	Isolation of p – xylene from m/p-mixtures	Distillate pre-separation of o – xylene and ethylbenzene from C ₈ aromatic fractions
Adsorption on solids	Isolation of p – xylene from C ₈ aromatics fractions	Continuous, reversible, and selective adsorption

a) **Azeotropic distillation:** The addition of strongly polar auxiliary agents (e. g. alcohols, ketons, water) facilitates the removal of alkanes and cycloalkanes. An assumption for

²⁷ IFP...Institut Francais du Petrole

the use of azeotropic distillation is that the fractions are narrow cuts, from which the non-aromatics are removed. In the case of the benzene fraction acetone is added whereas in the case of the toluene or xylene fraction methanol is used. In a further step the used auxiliary agent (e. g. acetone or methanol) is extracted with water, recovered by distillation and recycled to the azeotrope column.

- b) **Extractive Distillation:** Just as in the azeotropic distillation single, narrow cut fractions are used for the extractive distillation. The aromatic fraction is fed into the middle of the column, whereas the selective solvent is fed at the top. The non-aromatics leave the column at the top and the solvent with the aromatics is removed from the lower part. The bottom product, a mixture of solvent and pure aromatic, is separated in a distillation column into solvent and aromatic.

Compared to the azeotropic distillation where the auxiliary substance acts on the non aromatic fraction in extractive distillation the auxiliary agents acts on the aromatic fraction and decreases its volatility.

- c) **Liquid-liquid extraction:** This separation method is the more widely applied technique. Many different solvents and mixtures have been used in commercial processes. The numerous modifications of liquid-liquid extraction are all characterised by countercurrent operations. Normally an extraction column is used, where the mixture to be separated is fed in the middle of the column and the solvent is fed at the top of the column. The non-aromatics leave the column at the top, whereas the aromatics with the solvent are removed from the bottom. To improve the separation, part of the purified aromatics fraction is recirculated to the bottom of the extractor to force the non-aromatics completely from the extract. In a further step the extract has to be separated in the aromatics and the solvent. Two different possibilities are available for this separation step:

- Direct distillation, often with a steam strip.
- Re-extraction of the aromatics from the selective solvent with a light hydrocarbon such as pentane. From this solvent the aromatics are freed by a simple distillation. This method saves the expensive extractant and is energetically favorable.

The major difference between liquid-liquid extraction and extractive distillation is that in liquid-liquid extraction the extracting solvent must be as polar that at all stages a readily separable two liquid phase system is retained. In extractive distillation there is only one liquid phase.

Table 22 presents an overview of used processes and the solvents used in these processes.

Table 22: *Commercially used solvent extractions for production of aromatics [WINNACKER et al., 1981a] and [WEISSERMEL & ARPE, 1998d]*

process	solvent	company
Arosolvan	N-Methylpyrrolidone/H ₂ O	Lurgi
Udex	glycol	UOP – Dow
Sulfolane	sulfolane	Shell – UOP
Formex	N-Formylmorpholine/H ₂ O	SNAM – Progetti
Morphylex	N-Formylmorpholine/H ₂ O	Krupp – Koppers
DMSO	Dimethyl sulphoxide/H ₂ O	IFP
Arex	N-Methyl-ε-caprolactam	Leuna – Werke

The extraction- and the extractive distillation process use selective solvents, which solve the aromatics fraction better than the non-aromatics fraction. With increasing polarity of the solvent the selectivity of it is increasing, but its capacity decreases. Rests of the solvent in the raffinate (non-aromatics fraction) have to be separated and recycled.

Separation of the C₈ fraction:

The separation of the C₈ – fraction is very difficult. It mainly consists of o-, m-, p-xylene and ethylbenzene.

- a) **Crystallisation method:** Before the crystallisation could start o-xylene and ethylbenzene must be separated from the mixture because they can form eutectic systems with p-xylene. In the first step the high-boiling o-xylene is removed in a distillation column from the ethylbenzene/m-xylene/p-xylene mixture. In a further step ethylbenzene is separated by distillation. An intermediate fraction of m-xylene/p-xylene with a ratio of 2 : 1 remains. This fraction must be carefully dried to remove the water. For this Al₂O₃ or SiO₂ are used and after drying the water content of the mixture is approximately 100 ppm. This water free mixture is then cooled to temperatures between – 20 and – 75 °C and the p-xylene deposits on the cold walls. Then p-xylene is scraped from the cold walls by scrape chillers and removed as a crystal sludge. The crystal sludge is separated in a crystal cake and a filtrate by using filters or centrifuges. After the first stage of this process the crystal cake contains about 70 % of p-xylene. By using series of melting and crystallisation processes p-xylene could be obtained in 99.5 % purity.
- b) **Adsorption on solids:** An other method for the separation of p-xylene is the adsorption on solids. These solids must have such a surface and pore structure that they have an adsorption specificity for p-xylene. Two different processes gained in interest for commercial applications. The first process is the Aromax process. P-xylene is selectively adsorbed at modified zeolites (molecular sieves) from the liquid phase at 200 °C and 15 bar. The other process is the Parex process, which uses the same principle of adsorption on porous solid adsorbents. The adsorption is done at 120 to 175 °C in the liquid phase and the desorption is performed by washing with toluene or p-diethylbenzene. [WINNACKER et. al., 1981b]

3.2 Emissions

For the production of 1 000 kg benzene 1 136 kg crude oil as raw material is necessary. The total emissions for the production of benzene starting with the crude oil production are presented in Table 23. They are divided into atmospheric emission, waterborne emission and solid waste and based on calculations and data from industry.

Table 23: Emissions during the production of benzene in Europe (kg/t benzene) [FRANKE et al., 1995]

atmospheric emissions	emissions [kg/t]
particulates	0.37 kg/t
nitrogen oxides	2.82 kg/t
hydrocarbons	1.76 kg/t
sulphur oxides	2.97 kg/t
carbon monoxide	0.34 kg/t

atmospheric emissions	emissions [kg/t]
aldehydes	0.0063 kg/t
methane	0.001 kg/t
other organics	0.1 kg/t
ammonia	0.0028 kg/t
fossil CO ₂	649 kg/t
waterborne emissions	emissions [kg/t]
acid	0.014 kg/t
metal ions	0.0027 kg/t
fluorides	0.0025 kg/t
dissolved solids	0.77 kg/t
suspended solids	0.15 kg/t
BOD	4.89 kg/t
COD	0.059 kg/t
phenol	0.0027 kg/t
sulphides	0.0018 kg/t
oil	0.34 kg/t
hydrocarbons	0.0062 kg/t
solid waste	15.6 kg/t

The oil/water separator, which is used for wastewater treatment in refineries and in the petrochemical industry also separates benzene from the waste water, because of the high solubility of benzene in oil.

3.3 Use of the aromatics

Benzene:

Benzene is mainly used as raw material for the production of several products. For the year 1997 the benzene consumption is presented in Figure 9. It can be seen that the most important product from benzene is ethylbenzene. Other important products are cyclohexane and cumene. The importance of benzene for the production of maleic anhydride decreased significantly in the last 20 years (see also Chapter 4.4).

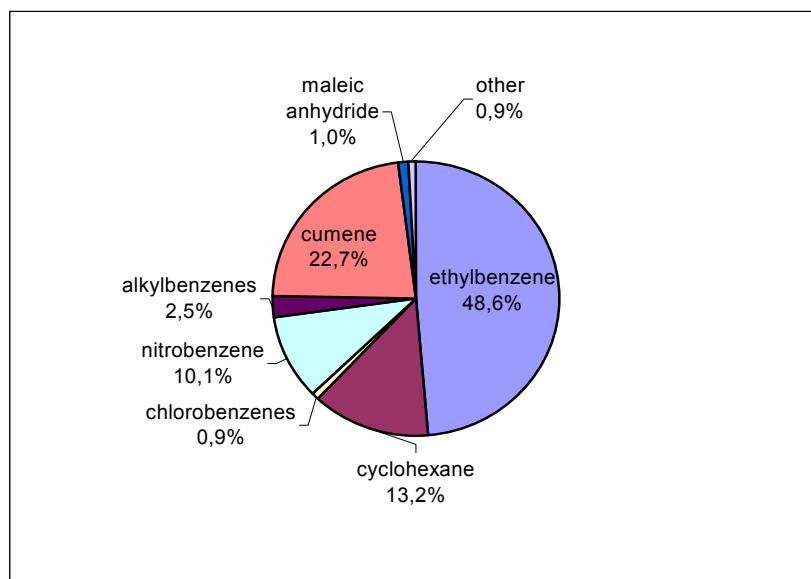


Figure 9: Use of benzene in Western Europe in 1997 [WWW.CEFIC.BE, 1999]

Table 24 presents the reaction partners of benzene for the production of the most important products of benzene.

Table 24: Products from benzene [WINNACKER et al., 1981c]

reaction partners	product
benzene + ethylene ⇒	ethylbenzene
benzene + propylene ⇒	cumene
benzene + H ₂ ⇒	cyclohexane
benzene + HNO ₃ ⇒	nitrobenzene
benzene + O ₂ ⇒	maleic anhydride

Toluene:

Toluene is used as a solvent, for addition to fuels to increase the octane number, for the production of benzene and for different chemical synthesis. Also benzene was substituted by toluene in the last years in several parts.

Xylene:

- p-xylene is used for the production of terephthalic acid and for the production of dimethyl terephthalate, which are both used as a feedstock to make polyesters for use in synthetic fibre, films, packaging materials and containers.
- o-xylene is used for the production of phthalic anhydride, a precursor for plasticizers.
- m-xylene is in little demand, except for oxidation to isophthalic acid.
- ethylbenzene is mainly used for the production of styrene, which is used for the production of polystyrene and other polymers.

3.4 Austria

In Austria pyrolysis petrol from the steam cracker, which mainly consists of aromatics is not separated into its different components. Only benzene is separated from the pyrolysis petrol up to concentrations of 80 % benzene by distillation. This fraction is further treated in an other refinery and upgraded to benzene concentrations of 99.9 % there.

The other aromatics such as toluene or xylene are not separated until now. The remaining rest of the pyrolysis gasoline after separation of the benzene fraction, including toluene and xylene is added to the petrol.

4 OXYGEN CONTAINING HYDROCARBONS

4.1 General Overview of Oxygenated Hydrocarbons

The following Chapter should give a short overview of groups of oxygen containing hydrocarbons. For each group some examples are mentioned that are produced in higher amounts. At the end of the chapter large volume organic chemicals containing oxygen, which are produced in Austria are listed.

Table 25: Overview of groups of oxygen containing hydrocarbons – examples for substances produced on large scale in the EC

	formation mechanism	raw materials
alcohols		
methanol	<ul style="list-style-type: none"> • high and low pressure processes 	CO + H ₂
ethylene glycol	<ul style="list-style-type: none"> • hydration of ethylene oxide 	C ₂ H ₄ O + H ₂ O
tertiary butanol	<ul style="list-style-type: none"> • direct hydration of isobutene • indirect hydration of isobutene • by-product during the production of propylene oxide (Oxirane process) 	C ₄ H ₈ + H ₂ O C ₄ H ₈ + H ₂ SO ₄ C ₃ H ₆ + C ₄ H ₁₀ + O ₂
2-ethylhexanol	<ul style="list-style-type: none"> • aldol condensation, as intermediate 2-ethylhexenal is formed from butyraldehyde 	2 butyraldehyde
isopropanol	<ul style="list-style-type: none"> • direct hydration of propylene • indirect hydration of propylene with H₂SO₄ 	C ₃ H ₆ + H ₂ O C ₃ H ₆ + H ₂ SO ₄
ethanol	<ul style="list-style-type: none"> • direct hydration of ethylene • indirect hydration of ethylene with H₂SO₄ • alcoholic fermentation 	C ₂ H ₄ + H ₂ O C ₂ H ₄ + H ₂ SO ₄
propylene glycol	<ul style="list-style-type: none"> • hydration of propylene oxide 	C ₃ H ₆ O + H ₂ O
aldehydes		
formaldehyde	<ul style="list-style-type: none"> • oxidation of methanol • oxidative dehydrogenation of methanol 	CH ₃ OH + ½ O ₂ CH ₃ OH + ½ O ₂
acetaldehyde	<ul style="list-style-type: none"> • oxidation of ethylene • oxidative dehydrogenation of ethanol 	C ₂ H ₄ + ½ O ₂ C ₂ H ₅ OH + ½ O ₂
ketones		
acetone	<ul style="list-style-type: none"> • oxidation of propylene • dehydrogenation of isopropanol • co-production in the Cumol – Process for phenol production 	C ₃ H ₆ + ½ O ₂ C ₃ H ₇ OH isopropylbenzene + O ₂
methyl ethyl ketone	<ul style="list-style-type: none"> • dehydrogenation of 2-butanol 	C ₄ H ₉ OH

	formation mechanism	raw materials
carboxylic acids		
terephthalic acid	<ul style="list-style-type: none"> • catalytic oxidation of p-xylene 	p-xylene + O ₂
acetic acid	<ul style="list-style-type: none"> • catalytic oxidation of acetaldehyde • oxidation of n-butane • catalytic oxidation of ethylene • carbonylation of methanol 	CH ₃ CHO + ½ O ₂ CH ₃ OH + CO
adipic acid	<ul style="list-style-type: none"> • catalytic oxidation of cyclohexanol/cyclohexanone with HNO₃ • catalytic oxidation of cyclohexanol/cyclohexanone with air 	
acrylic acid	<ul style="list-style-type: none"> • catalytic oxidation of propylene via the intermediate acrolein 	C ₃ H ₆ + O ₂
citric acid	<ul style="list-style-type: none"> • fermentation 	
anhydrides		
acetic anhydride	<ul style="list-style-type: none"> • oxidation of acetaldehyde • ketene process 	2 CH ₃ CHO + O ₂ CH ₃ COOH + CH ₂ =C=O
phthalic anhydride	<ul style="list-style-type: none"> • oxidation of o-xylene • oxidation of naphthalene 	o-xylene + 3 O ₂ naphthalene + 9 O ₂
maleic anhydride	<ul style="list-style-type: none"> • oxidation of benzene • oxidation of butene • oxidation of n-butane 	benzene + 4.5 O ₂ butene + 3 O ₂ n-butane + 3.5 O ₂
esters		
dimethyl terephthalate	<ul style="list-style-type: none"> • esterification of terephthalic acid and methanol 	
vinyl acetate	<ul style="list-style-type: none"> • oxidation of ethylene • catalytic addition of acetylene to acetic acid 	C ₂ H ₄ + ½ O ₂ + CH ₃ COOH C ₂ H ₂ + CH ₃ COOH
acrylate	<ul style="list-style-type: none"> • esterification of acrylic acid with different alcohols 	acrylic acid + CH ₃ OH or C ₂ H ₅ OH and so on
ethyl acetate	<ul style="list-style-type: none"> • esterification of acetic acid and ethanol • from acetaldehyde with the Tishchenko reaction 	CH ₃ COOH + C ₂ H ₅ OH 2 CH ₃ CHO
ethers		
MTBE	<ul style="list-style-type: none"> • addition of methanol to isobutene 	CH ₃ OH + C ₄ H ₈

	formation mechanism	raw materials
epoxides		
ethylene oxide	• catalytic oxidation of ethylene	$C_2H_4 + \frac{1}{2} O_2$
propylene oxide	• indirect oxidation of propylene (Oxirane process) • chlorohydrin process	$C_3H_6 + C_4H_{10} + O_2$ $2 C_3H_6 + 2 HOCl + Ca(OH)_2$
others		
phenol	• Cumol – Process	isopropylbenzene + O_2

4.1.1 Production of Oxygen Containing Hydrocarbons in Austria

Table 26: Oxygen containing hydrocarbons that are produced in Austria

	annotations	capacity [t/a]
alcohols		
diols	• special diols e. g. 1,2-pentandiol or 1,2-hexandiol	small amounts
aldehydes		
formaldehyde	• oxidative dehydrogenation of methanol	91 000 t/a
carboxylic acids		
citric acid	• fermentation	
fumaric acid	• isomerization of maleic acid	
butanedioic acid	• hydrogenation of maleic acid	
glyoxylic acid	• ozonolysis of dimethyl maleate	14 990 t/a
peracetic acid	• oxidation of acetic acid with H_2O_2	4 000 t/a
anhydrides		
phthalic anhydride	• oxidation of o-xylene	50 000 t/a
maleic anhydride	• oxidation of n-butane	30 000 t/a
esters		
	• a lot of different esters of maleic acid, fumaric acid and butanedioic acid with isopropanol, methanol,...	
ethers		
MTBE	• addition of methanol to isobutene	67 000 t/a
epoxides		
	• special epoxides as e. g. cyclooctenoxid or 1-hexenoxid	small amounts

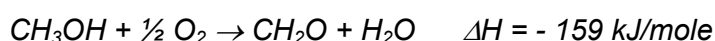
4.2 Formaldehyde

4.2.1 Production Processes of Formaldehyde

The production processes of formaldehyde can be divided into two groups due to the type of chemical reaction, which is used in the process. One kind of processes use the oxidative dehydrogenation of methanol whereas the other processes use oxidation of methanol.

a) Oxidative Dehydrogenation of Methanol

Methanol and air are led over a silver catalyst (silver crystal or gauze) at temperatures between 500 and 700 °C. A less than stoichiometric amount of air is used in the industrial process. The yield of formaldehyde strongly depends on the reaction temperature of the process.



The residence time over the catalyst must be very short (< 0.01 s) because formaldehyde is decomposed into carbon monoxide and hydrogen at temperatures higher than 400 °C. After the catalyst, the formed formaldehyde is cooled down immediately to approximately 150 °C. A measure to reach a constant temperature in the reactor is the injection of water. The injection of water has different positive effects. On the one side it is easier to regulate the temperature range for the reaction, on the other side the lifetime of the catalyst is increased. Normally the catalyst has a lifetime of 2 – 4 months and the spent catalyst can be easily regenerated electrolytically without loss of silver. The third advantage of water injection is an increased turnover of methanol in the presence of water.

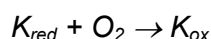
Processes working at temperatures between 515 and 650 °C (ICI, Monsanto or Degussa) reach methanol turnovers between 77 and 87 %. Due to this a recovery of the not converted methanol is necessary in a distillation column.

The process of BASF uses higher temperatures (680 to 720 °C) and thus a nearly complete transformation of methanol is reached. Methanol recovery is not necessary if this process is used.

Formaldehyde is washed out from the exhaust gas with water, which leads to a formaldehyde solution (37 – 44 %). The solution is stabilised towards polymerisation with a residual amount of methanol (1 – 2 %). After the separation of formaldehyde the exhaust gas contains N₂, H₂, H₂O, CO₂, methanol and a formaldehyde rest. This gas is combustible and could be used for steam production and for the generation of electricity.

b) Oxidation of Methanol

Methanol is oxidized with atmospheric oxygen to formaldehyde and water. Catalysts used for this process are iron oxide (Fe₂O₃ 18 – 19 %) and molybdenum oxide (MoO₃ 81 – 82 %). The reduced catalyst is simultaneously regenerated with atmospheric oxygen. The lifetime of this catalyst is approximately two years.



At a temperature of about 350 °C nearly the whole methanol is oxidized. One important by-reaction is the oxidation of formaldehyde to CO₂ and H₂O.

The most important process of methanol oxidation nowadays is the Formox process developed by Perstop and Reichhold. A mixture of air and methanol (approximately 8 Vol%) is mixed with steam and then feed to a tube bundle reactor with a fixed bed catalyst. The temperature increases due to the exothermic reaction from 220 °C to 320 °C. Reaction heat is discharged by indirect cooling. After the reaction, reaction gas is immediately cooled down to approximately 110 °C. This heat can be used for steam generation. The separation of formaldehyde from the reaction gas is made in a multi-stage absorption process with water. The solution contains 37 – 60 % formaldehyde, ~ 1 % methanol and small amounts of formic acid (0.05 %). The formic acid can be removed in a coupled ion exchanger.

The exhaust gas of this process is not combustible due to the high excess of air. For further treatment it is incinerated with additional natural gas.

Wastewater containing formaldehyde could be converted to methanol and sodium formate by the addition of alkalis at higher temperatures.

To remove formaldehyde and methanol from the exhaust gas, incineration seems to be the best technology. Using oxidative processes natural gas has to be added to the exhaust gas for incineration.

4.2.2 Use of Formaldehyde

A lot of different applications of formaldehyde exist. Direct applications of aqueous formaldehyde solutions are as disinfectant and preservative. It is also the raw material for a lot of products. Some examples are:

- urea resins;
- phenol resins;
- melamine resins.

The worldwide capacity for formaldehyde production was 4.9 x 10⁶ tonnes per year. The largest single plants have capacities up to 200 000 tonnes per year. Table 27 shows the development of formaldehyde production in different states and regions.

Table 27: HCHO Production in Western Europe, USA, BRD and Japan [WEISSERMEL & ARPE, 1998]

	1989	1991	1992
Western Europe	1 300 000 t	1 370 000 t	1 400 000 t
USA	780 000 t	810 000 t	860 000 t
Germany	680 000 t	600 000 t	670 000 t
Japan	360 000 t	390 000 t	380 000 t

4.2.3 Austria

In the Austrian plant at Krems - Chemie dehydrogenation of methanol is used for the production of formaldehyde. A solution of methanol in water (65-weight per cent methanol) is evaporated with air. For the reaction silver crystals are used as catalysts. Only a small layer (15 – 20 mm) of catalyst is necessary and the reaction time is very short (in the order of 0.001 s). The small layer of catalyst consists of particles with different diameters. The reaction takes place in the upper part of the catalyst layer with the smaller catalyst particles. The lifetime of the catalyst is between six weeks and six months depending on the reaction conditions. The used catalyst is regenerated with electrolysis by the Krems - Chemie itself. During the exchange of the catalyst revisions and maintenance work are made. For this approximately five times a year the plant stands still for 24 hours. During the cleaning of the plant approximately 1 – 2 m³ of waste water are formed. For the cleaning caustic soda and nitric acid are used.

After the reaction, the reaction gas is immediately cooled down and then formaldehyde is separated in an absorber with water. At the head of the absorber a solution of methanol is discharged and recirculated to the reactor.

The capacity of all plants is 91 000 tonnes per year calculated as hundred percent formaldehyde. This corresponds to a capacity of 250 000 tonnes per year related to a formaldehyde solution with 36.5 % formaldehyde. The annual production in 1998 was 83 600 tonnes of formaldehyde (100 %) or 229 000 tonnes of a 36 % solution of formaldehyde. For the production of these amounts 102 000 tonnes methanol were used in 1998.

After the separation of formaldehyde in the absorber with water the exhaust gas contains small amounts of hydrogen (15 – 20 %). Table 28 presents the composition of the exhaust gas after the absorber.

Table 28: Exhaust gas composition after the absorber [KREMS Chemie, 1999]

component	concentration
H ₂	15 – 20 Vol. %
H ₂ O	2 – 4 Vol. %
CO ₂	4 – 5 Vol. %
CO	0.1 – 0.3 Vol. %
methanol	100 – 1000 ppm
formaldehyde	10 – 20 ppm

Former all of the exhaust gas was incinerated for steam production. Nowadays the main part of this lean gas is used for the production of electricity. In 1998 approximately 142 Mio. Nm³ lean gas were produced during formaldehyde production. Approximately 91 Mio. Nm³ were used for the production of electricity. The rest was used for steam production in steam boilers. In general additionally natural gas is incinerated in the steam boilers for steam production (see also emission data of the steam boilers). The low energy content of the lean gas was a technologically solvable problem. The power plant of Krems - Chemie consists of four components.

- Four gas engines with downline generators and steam boilers for utilisation of the exhaust gas heat;
- An additional waste heat boiler in formaldehyde plant 5;
- A steam storage tank for equalisation of peaks during steam consumption;

- A process control system for optimal regulation of all systems.

The lean gas burned in the four engines has a very low calorific value of approximately 2000 kJ/m³. Downline generators produce electricity. Each engine has an exhaust gas catalytic converter, especially to oxidize the CO of the exhaust gas. Two engines are coupled with one steam boiler using the waste heat of the exhaust gas for steam production. The boiler feed water is pre-heated by the engine cooling water. 75 % of the electricity requirements of the Krems - Chemie can be recovered. Due to the low combustion temperatures the formation of NO_x is low. The exhaust gases of the engines are led over oxidation catalysts to reduce the CO content. Additionally the content of nonburned H₂ is reduced in the oxidation catalysts. Table 29 presents as an example the emissions of one of these four gas engines.

Table 29: Composition of the exhaust gas of one gas engine [PUXBAUM & ELLINGER, 1997a]

time	CO	NO _x	total C
16:00-16:30	57 mg/m ³	12 mg/m ³	10 mg/m ³
16:30-17:00	59 mg/m ³	11 mg/m ³	10 mg/m ³
17:00-17:30	50 mg/m ³	14 mg/m ³	10 mg/m ³
mean value	55 mg/m³	12 mg/m³	10 mg/m³

All these values are related to an oxygen content of 5 Vol. % and to dry exhaust gas at normal state (0 °C and 1 013 mbar). The permitted values for this unit are 100 mg/Nm³ NO_x and 150 mg/Nm³ CO.

The amount of energy input into the gas engines is the volume flow of the lean gas multiplied by the calorific value. The usable forms of energy are the generated electricity, the produced steam and the pre-heated feed water. The remaining energy is lost via the mixture cooler, oil- and water cooler and by radiation of the engines [KREMS Chemie, 1998].

- Electrical power output: 2 352 kW
electrical efficiency: 34 %
- Generated steam (10 bar): 1 300 kg/h (855 kW)
- Pre-heated feed water: 12 000 kg/h (ΔT = 60 °C, 835 kW)
- Degree of heat utilisation: 23 – 33 %
- Total energy utilisation: 57 – 67 %

The costs for the power plant, the steam storage tank and the additional waste heat boiler have been approximately 50 Mio. ATS.

The rest of the lean gas, which is not used for the generation of electrical power, is used for steam production in two flame tube boilers. In total 105 000 tonnes steam were produced in 1998 in the formaldehyde plant. The main part is from the waste heat boilers of the production plant. The rest is produced during the incineration of the rest of the lean gas and from the use of waste heat, which is formed during the generation of electricity in the gas engines. Sometimes natural gas is additionally used in the steam production in the flame tube boilers (three pass boilers).

The permitted emission standards for the two steam boilers used at the Krems Chemie are presented in the following Table. The emission standards have to be related to an oxygen content of 3 Vol. % and to dry exhaust gas at normal state (0 °C, 1 013 mbar).

Table 30: Emission standards for the two steam boilers at the Krems Chemie [PUXBAUM & ELLINGER, 1998]

pollutant	emission standard
dust	10 mg/m ³
carbon monoxide	100 mg/m ³
NO _x	200 mg/m ³
organic carbon	20 mg/m ³

In the following two Tables the emissions of the two steam boilers are presented. The boiler 3 was built in 1998 and during the measurements additionally natural gas was incinerated. During the measurement time of 2.5 hours the volume flow of natural gas differed between 126 and 128 m³/h and the volume flow of lean gas differed between 4 578 and 4 825 m³/h.

Table 31: Emissions from the steam boiler 3 [PUXBAUM & ELLINGER, 1998]

time	CO	NO_x	total carbon	dust
10:00-10:30	< 2 mg/m ³	22 mg/m ³	< 2 mg/m ³	-
10:30-11:00	69 mg/m ³	20 mg/m ³	14 mg/m ³	< 2 mg/m ³
11:00-11:30	< 2 mg/m ³	21 mg/m ³	< 2 mg/m ³	< 2 mg/m ³
11:30-12:00	< 2 mg/m ³	21 mg/m ³	< 2 mg/m ³	< 2 mg/m ³
12:00-12:30	< 2 mg/m ³	21 mg/m ³	< 2 mg/m ³	-
mean value	< 2 mg/m³	21 mg/m³	< 2 mg/m³	< 2 mg/m³

Again all measurements are related to 3 Vol. % remaining oxygen and to dry gas at standard conditions. In the time of 10:33-10:38 the burner was turned off due to a disturbance. The half-hour mean value of 10:30-11:00 was thus not used for the formation of mean value.

The steam boiler 2 was built in 1962. During the measurement time (3 hours) approximately between 2 800 and 3 600 Nm³/h lean gas were burned. Additionally 1 to 2 m³/h natural gas were used.

Table 32: Emissions from the steam boiler 2 [PUXBAUM & ELLINGER, 1997b]

time	CO	NO_x	total carbon
12:46-13:16	87 mg/m ³	< 2 mg/m ³	< 2 mg/m ³
13:16-13:46	82 mg/m ³	2 mg/m ³	< 2 mg/m ³
13:46-14:16	82 mg/m ³	3 mg/m ³	< 2 mg/m ³
14:16-14:46	98 mg/m ³	5 mg/m ³	< 2 mg/m ³
14:46-15:16	72 mg/m ³	6 mg/m ³	< 2 mg/m ³
15:16-15:46	52 mg/m ³	7 mg/m ³	< 2 mg/m ³
mean value	79 mg/m³	4 mg/m³	< 2 mg/m³

A comparison of the emission data of the two steam boilers shows the influence of the amount of natural gas, which is added. The higher amount of natural gas added in steam

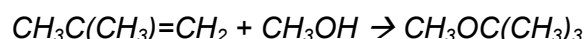
boiler 3 leads to much higher emission values for NO_x (factor 5 if the mean values are compared), but much lower emission values for CO. The emissions of total carbon are not affected by the addition of natural gas.

4.3 MTBE

Three different possibilities for the commercial production of MTBE exist. The most important process is the production of MTBE from isobutene of the C₄ fraction of the steam cracker. Approximately 82 % of the total produced isobutene is used for MTBE production. Other possibilities are the dehydrogenation of isobutane and the oxidation of isobutane.

4.3.1 Production of MTBE from Isobutene

MTBE is formed by the addition of an alcohol (methanol) to an olefin (isobutene).



The reaction between methanol and isobutene takes place in the liquid state and at temperatures between 30 and 100 °C and a slight excess pressure. Acid ion exchange resins are used as catalysts. The C₄ raw material can be the C₄ fraction from the steam cracking process after butadiene was separated or selectively hydrogenated and/or the C₄ fraction from a FCC unit. The amount of isobutene is between 44 and 50 % in the C₄ mixture of a steam cracker and approximately 20 % from a FCC Unit. The other raw material is methanol, which is added with an over stoichiometric amount. Normally two reactors are used for the production process having different pressure (5 – 8 bar) and temperature (40 – 70 °C) levels but also a two-stage shaft reactor can be used. The turnover of isobutene reaches values between 98 to 99.8 % under these conditions. By-products of this reaction are di-isobutene and tertiary butanol.

The separation of the product mixture (MTBE, methanol and C₄ fraction) is very difficult because they form an azeotropic mixture. First the mixture is distilled in a pressurized column (9 bar). The remaining C₄ fraction (e. g. n-butenes, butane or isobutane) forms the top product, whereas methanol and MTBE are discharged at the bottom. In the second column MTBE and methanol are separated at 130 °C. The bottom product consists of 99 % MTBE whereas the top product contains 30 % methanol and 70 % MTBE. This top product is recirculated to the reactor.

In an alternative separation scheme the reactor product is separated in a pressurized distillation column (5 to 6 barg) into a mixture containing all C₄'s and methanol with only small amounts of MTBE leaving from the top of the column (45 °C) and the finished MTBE product leaving from the bottom of the column (125 °C). Methanol is extracted from the C₄-rich stream by means of water in an extraction tower (10 barg, 40 °C). In a second distillation column methanol (top 0.8 barg, 45 °C) is separated from water (bottom 1.25 barg, 124 °C) and sent back to the reactor. The water is routed back to the extraction column. In this scheme no MTBE is recirculated to the reactor.

During the reaction of isobutene with methanol as described above, all the other components of the C₄ fraction remain unchanged.

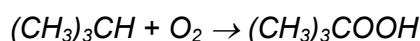
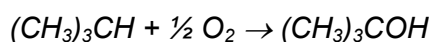
4.3.2 Production of MTBE by Dehydrogenation of Isobutane

Due to the increasing demand for MTBE new technologies are developed to produce enough MTBE. One process is the dehydrogenation of isobutane to isobutene with subsequent formation of MTBE with methanol. Disadvantages of this process are the high energy requirements due to the endothermic dehydrogenation reaction and the coke formation on the catalysts. For regeneration of the catalysts, the coke has to be removed from the catalysts by incineration.

A new process design allows a simultaneous and continuous reaction and regeneration. The dehydrogenation is conducted in the first vessel, a bubbling staged fluidized bed using a promoted chromia/alumina catalyst. The spent catalyst, due to coke formation, is withdrawn from the bottom and pneumatically brought to the second vessel. Here coke is burnt off heating up the solid inventory which supplies the reaction heat of the endothermic reaction. [ROSSINI et al., 1998]

4.3.3 Production of MTBE by Oxidation of Isobutane

Another possibility for MTBE production is the liquid phase oxidation of isobutane. In a first step tertiary butanol and tertiary butyl-hydroperoxide are formed from isobutane in the liquid phase. Then the tertiary butanol and methanol form MTBE and water. By-products during the oxidation reaction are acetone, CO₂ and methanol.



The peroxide has to be decomposed before the product stream is separated because of safety requirements. The decomposition is made under hydrating conditions on heterogeneous catalysts. Then the product stream is separated in isobutane, which is recirculated to the oxidation stage and a product consisting of tertiary butanol, acetone, methanol and water. In a second rectification step acetone and methanol are separated from tertiary butanol and water. The water is not separated from tertiary butanol because in the next step (formation of MTBE from tertiary butanol) water is produced. [BREJC et al., 1994]

4.3.4 Production and Use of MTBE

Since the 70's the importance of MTBE is growing. It is mainly used as a blending component for gasoline production to compensate for octane losses due to reformulation and to enhance the combustion behaviour. Table 33 shows the development of the MTBE production in different economic regions. The increase in Japan and USA is much higher than in Western Europe.

Table 33: Development of the MTBE production in different economic regions (tonnes)
[WEISSERMEL & ARPE, 1998]

	1991	1993	1995
USA	4 350 000 t/a	5 550 000 t/a	7 990 000 t/a
Western Europe	2 420 000 t/a	2 530 000 t/a	2 670 000 t/a
Japan	80 000 t/a	290 000 t/a	410 000 t/a

4.3.5 Austria

Since 1983 in Austria one plant for MTBE production exists. The applied process uses the C₄ fraction of the steam cracker (freed from butadiene) as well as the olefinic C₄ stream of the FCC unit as raw material and ion exchangers as catalysts. The capacity of the plant is 67 000 t/year. 50 000 to 60 000 tonnes per year are produced there. The waste water is cleaned in the sewage treatment plant. The remaining C₄ fraction (Raffinate 2) is not changed during the process and used as blending component for gasoline production or is utilised as steamcracker feed.

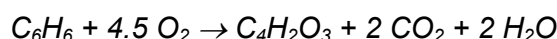
4.4 Maleic Anhydride

For the production of maleic anhydride, processes using different raw materials exist. In the 1960s benzene was the only raw material for maleic anhydride production. Since this time the input materials changed significantly. In 1991 36 % of the maleic acid capacity was still based on benzene. The rest of the capacity was based on C₄ compounds especially butane and butene. The reasons for this change may be the stricter emission standards for benzene and the decreasing prices for raw materials as butane and butene.

4.4.1 Production Processes

4.4.1.1 Oxidation of Benzene

Benzene is fed to a pre-heated air stream and thus a homogeneous mixture of the input material is achieved. A high amount of excess air is used for the oxidation. Most of the reactors use a fixed bed of catalysts for the reaction, but fluidized bed reactors as well are in use now. All different processes for benzene oxidation use similar catalysts based on V₂O₅ which may be modified with for example MoO₃. Due to the high exothermic reaction normally tube bundle reactors with up to 13 000 externally cooled tubes are used. Fused salts are used as circulating heat exchange liquid to remove the reaction heat and to produce steam. Not the whole amount of the reaction heat could be recovered (approximately 80 % can be used for steam production). The oxidation of the benzene/air mixture takes place at 350 – 450 °C and 1.5 – 2.5 bar with residence times over the catalysts of about 0.1 s.



In a typical conversion of 100 mole benzene 73 mole maleic anhydride are produced. 23 mole of the benzene is completely oxidized to CO₂ and H₂O and the rest (4 mole or 43.65 kg/t maleic anhydride) reach the exhaust gas [ULLMANN's, 1978]. This amount of benzene has to be recovered by adsorption on e. g. activated carbon and reused in the production process.

In the year 1986 the maleic anhydride production was the biggest source for benzene emissions in the chemical industry [BUA, 1988]. 3.3 to 20.4 kg benzene were emitted per tonne benzene used for the production of maleic anhydride. The situation should be better now due to improved strategies of benzene removal and recirculation from the exhaust gas. Table 34 presents the composition of uncontrolled emissions from the product recovery absorber.

Table 34: Composition of uncontrolled emissions from the product recovery absorber

Component	Amount [kg/t]
Nitrogen	21 406 kg/t
Oxygen	4 863 kg/t
Water	1 167 kg/t
Carbon dioxide	972 kg/t
Carbon monoxide	680 kg/t
Benzene	67 kg/t
Formaldehyde	14.4 kg/t
Maleic acid	2.8 kg/t
Formic acid	2.8 kg/t

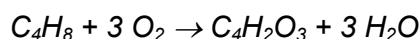
For the separation of maleic anhydride from the reaction gas mixture the reaction gas is cooled in several heat exchangers. In the last cooler the temperature is below the condensation temperature of the anhydride and 50 to 60 % of the anhydride is obtained directly from the reaction gas mixture. The remaining rest is washed out with water in the product recovery absorber in the form of maleic acid.

The 40 percent maleic acid is converted to maleic anhydride, usually by azeotropic distillation with xylene. Some processes may use a double effect vacuum evaporator at this point. The effluent then flows to the xylene stripping column where the xylene is extracted. Emissions of xylene from the vacuum pumps and the column have to be taken into account.

Fugitive emissions of benzene, maleic acid and maleic anhydride also arise from the storage and the handling of these substances.

4.4.1.2 Oxidation of Butene

In this process the feedstocks for maleic anhydride oxidation are butenes, which are by-products from butane dehydrogenation to butadiene or the C₄ – fraction of steam crackers. From this C₄ – fraction butadiene is separated and used as raw material for other products. The principle of butene oxidation is very similar to the oxidation of benzene. Again fixed bed tube reactors with a catalyst based on V₂O₅ are used. The reaction takes place at 350 – 450 °C and 2 – 3 bar.



Important by-products of this reaction are CO₂, CO, formaldehyde, acetic-, acrylic-, fumaric-, crotonic- and glyoxylic acid. An other process using the oxidation of butene for maleic anhydride production uses a V₂O₅ – H₃PO₄ catalyst, which is whirled in a fluidized bed. The big advantage of this process is the more facile heat removal at constant reaction temperatures. In contrast to benzene oxidation in the work up no partial condensation of maleic anhydride takes place. The reaction gas is washed with dilute aqueous maleic acid solution. Then the dilute maleic acid solution is concentrated under vacuum or with the help of water entraining agents. The exhaust gas contains 10 to 20 % of the initial hydrocarbons that could be removed by incineration. Again the emissions from the dehydration units have to be taken into account.

4.4.1.3 Oxidation of Butane

N-butane is the most economical raw material for maleic anhydride production. The process conditions are similar to those for benzene oxidation. Again the catalysts are based on vanadium oxides, but they differ in the promoters such as phosphor and the oxides of Fe, Cr, Ti, Co, Ni, Mo and other elements. Fixed bed processes as well as fluidized bed processes are established until now. One example for a fluidized bed process is the ALMA process. In this process n-butane is oxidized with air in a fluidized bed. Exothermic reaction heat is removed from the reactor producing high pressure steam in coil bundles located within the fluidized bed. Again the emissions from the dehydration units have to be taken into account. A detailed description of a plant using butanes as raw material is given in the Chapter about Austria.

4.4.1.4 By-Product during Phthalic Anhydride Production

A small amount of maleic anhydride could be produced as by-product during the production of phthalic anhydride.

4.4.2 Use of Maleic Anhydride

Maleic anhydride is used for the production of unsaturated polyesters, the production of fumaric- and malic acid, as intermediate for the production of pesticides, fungicides, insecticides and herbicides and as an additive for lubricating oil. Table 35 presents the development of the use of maleic anhydride from 1986 to 1995.

Table 35: Development of the use of maleic anhydride [WEISERMEL & ARPE, 1998]

product	USA		Western Europe		Japan	
	1986	1995	1986	1995	1986	1995
unsaturated polyesters	57 %	64 %	56 %	50 %	41 %	32 %
fumaric/malic acid	10 %	3 %	4 %	10 %	14 %	11 %
plant protectives	10 %	3 %	2 %	1 %	3 %	3 %
lubricating oil additives	9 %	11 %	5 %	6 %	3 %	3 %
others ²⁸	14 %	19 %	33 %	33 %	39 %	51 %
total consumption	164 000 t	206 000 t	157 000 t	201 000 t	64 000 t	104 000 t

4.4.3 Austria

Since 1993 in Austria one plant for maleic anhydride production exists, using n-butane as raw material. Before 1993 only benzene was used as raw material. In 1994 the last plants using benzene were shut down.

The plant based on butane as raw material was designed for a capacity of 30 000 t/a, but only outputs between 17 000 and 21 000 t/a are achievable according to an official of DSM Chemicals. Due to the higher demand of maleic anhydride, one of the older plants, formerly using benzene started again with the production in autumn 1999, using butane as raw material now instead of benzene.

The main difference between the two plants is that one plant uses a fluidised bed reactor, whereas the reactivated plant uses a fixed bed reactor. The total production of the fluidized bed plant and the fixed bed plant is 26 000 t/a. For this amount of maleic anhydride 39 200 t/a butane are needed as input material.

Fluidised bed process: (since 1993) The heat is removed from the fluidized bed by production of steam (50 bar). Approximately 40 t/h steam are produced during the maleic anhydride production. A vanadium phosphor compound is used as catalyst in this process. Smaller amounts of the catalyst are exchanged continuously, whereas larger amounts are exchanged in batch quantities. The removed catalyst is recycled as a source of vanadium.

The maleic anhydride is washed out from the reaction gases with water in the product recovery absorber in the form of maleic acid.

The exhaust gas after the scrubber is incinerated because it contains part of the unreacted input material butane and carbon monoxide. The exhaust gas incineration leads to the following emissions.

²⁸ e. g. production of γ -butyrolactone, 1,4-butanediol

Table 36: Emissions from the exhaust gas incineration of the fluidised bed reactor for maleic anhydride production [DSM Chemie Linz GmbH, 1998] and [DSM Fine Chemicals Austria, 2000]

component	1998		1999		emission standard
	concentration	amount	concentration	amount	
H ₂ O	185 000 mg/Nm ³	57 378.86 t/a	188 000 mg/Nm ³	59 330.92 t/a	–
CO ₂	255 000 mg/Nm ³	79 089.78 t/a	259 000 mg/Nm ³	81 737.81 t/a	–
CO	37 mg/Nm ³	11.48 t/a	3 mg/Nm ³	0.79 t/a	100 mg/Nm ³
NO _x	7 mg/Nm ³	2.17 t/a	7 mg/Nm ³	2.21 t/a	30 mg/Nm ³
TOC	4 mg/Nm ³	1.24 t/a	3 mg/Nm ³	0.79 t/a	5 mg/Nm ³

The emission standards are related to dry exhaust gas and an oxygen content of 3 Vol. %. The concentration of NO_x is calculated as NO₂. The waste heat of the exhaust gas is used for steam production (22 t/h; 50 bar).

For dehydration of the maleic acid solution the dehydration units of the older maleic anhydride plants are used and additionally a new dehydration plant was built. In the first step of the dehydration unit the solution is distilled with o-xylene. In a second step the raw maleic anhydride – xylene mixture is post-dehydrated and then in the last step pure maleic anhydride is produced by distillation. Uncontrolled xylene emission (~ 60 t/a) from the vacuum pumps of the dehydration unit arose, until the fixed bed plant was reactivated in autumn 1999. Since then the xylene emissions are collected and incinerated in the new regenerative firing of the restarted plant.

Fixed bed process: The plant, which was reactivated in autumn 1999 uses a fixed bed reactor instead of the fluidised bed reactor. As catalyst vanadium – phosphor – oxide is used in the reactivated plant.

First the overheated butane steam is mixed with process air, led over the catalyst and converted to maleic anhydride. The reaction heat is removed with a salt bath. Then the reaction gas is cooled and partially condensed (40 – 50 % of the maleic anhydride). The resulting gas is washed with water and the exhaust gas of the scrubber is mixed with air and then incinerated in a regenerative firing. This regenerative firing is used for exhaust gas treatment in the reactivated plant. The waste heat of the regenerative firing is currently not recovered.

The emission standards for the regenerative firing are presented in Table 37. The emission standards are related to an oxygen content of 11 Vol. % and dry exhaust gas at 0 °C and 1013 mbar. The measurement of organic carbon has to be made continuously.

Table 37: Emission standards for the regenerative firing of the exhaust gases of maleic anhydride production [ANU, 1999]

component	emission standard
CO	80 mg/m ³
NO _x (calculated as NO ₂)	20 mg/m ³
organic carbon	15 mg/m ³

Additionally to the exhaust gas of the reactors, the emissions of the dehydration unit are incinerated in this new regenerative firing. Due to the collection of xylene from the vacuum

pumps and the incineration of it in the regenerative firing no more relevant xylene emissions are expected in the future.

The former main sources of xylene emissions are presented in Table 38. The values are due to measurements of the Amt für Natur- und Umweltschutz (ANU).

Table 38: Sources of xylene emissions in the dehydration unit of the maleic anhydride plant [ANU, 1999]

source	mass flow	concentration	emission
dehydration column I	23.6 m ³ /h	64.4 g/m ³	1.54 kg/h
dehydration column II	51.5 m ³ /h	45.4 g/m ³	2.46 kg/h
xylene column	73.9 m ³ /h	54 g/m ³	4.03 kg/h
residue separation and post distillation	33.1 m ³ /h	0.2 g/m ³	0.01 kg/h
pure maleic anhydride column	23.7 m ³ /h	0.2 g/m ³	0.01 kg/h
condenser	-	79 g/m ³	-
condenser	7.5 m ³ /h	62 g/m ³	0.47 kg/h
sum			8.52 kg/h

The main by-products of maleic anhydride production are CO₂ (9 t/h) and fumaric acid (52 kg/h). Also a certain amount of waste water is produced. Approximately 4 m³/h with a COD – value of 25.5 g/l are removed from the process and treated at the general waste water treatment plant of the site.

The main part of the produced maleic anhydride is used for the production of unsaturated resins, fumaric acid and glyoxylic acid.

4.5 Phthalic Anhydride

Phthalic anhydride is a white solid and slightly soluble in water after hydrolysis. The world-wide consumption of phthalic anhydride reached approximately 3 000 000 tonnes in 1996, and is projected to reach 3.58 million t/a by 2001. Approximately 20 plants for phthalic anhydride production exist in Europe. The development of capacity and production data for phthalic anhydride in Western Europe (excluding Greece and Switzerland) from 1993 to 1997 is presented in Table 39.

Table 39: Development of capacity and production data for phthalic anhydride in Western Europe [www.cefic.be, 1999]

	1997	1996	1995	1994	1993
capacity	876 000 t	860 000 t	836 000 t	791 000 t	945 000 t
production	780 000 t	774 000 t	685 000 t	782 000 t	754 000 t

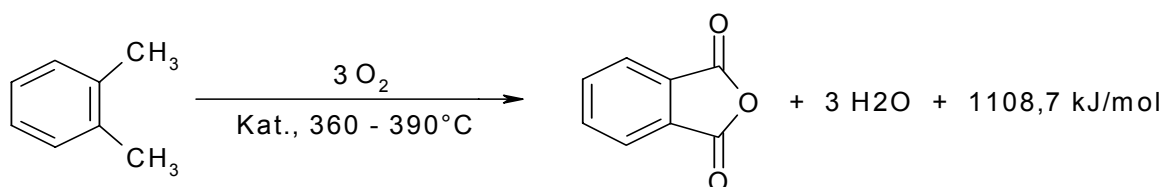
Phthalic anhydride is a very reactive component. The most important reactions of phthalic anhydride are esterifications with alcohols. These reactions lead to plasticizer or saturated and unsaturated polyester resins.

Two different raw materials for phthalic anhydride production exist. The first possibility is the production from naphthalene, but the importance of naphthalene decreased in the last decades. Nowadays o-xylene is the major feedstock, whereas naphthalene's use as a feedstock has diminished to about 16 % of the total [www.process-economics.com, 1998].

4.5.1 Production Processes of Phthalic Anhydride

Most of the processes with o-xylene use tube reactors for the oxidation. Different catalysts have been developed to improve the efficiencies of the processes. The oxidation of o-xylene could be made in the gas phase or in the liquid phase. The yield of a commercial plant using processes, which work in the gas phase, is between 105 – 109 kg phthalic anhydride per 100 kg o-xylene input. This is equivalent with 76 – 78 % of the theoretical output. Processes, which work with o-xylene in the liquid phase, reach yields of about 90 % of the theoretical values.

The reaction equation for the oxidation of xylene can be seen in the next figure.



a) Oxidation in the Gas Phase

For the oxidation in the gas phase three different processes exist. The mentioned Von Heyden process could use o-xylene or naphthalene as raw material for the oxidation.

- **Process of Rhône - Poulenc**

O-xylene is mixed with air and then oxidised in a tube reactor, which is filled up with catalysts. There o-xylene is oxidised to phthalic anhydride. After pre-cooling of the reaction gas in two heat exchangers phthalic anhydride is sublimated in a ripped tube separator. The molten raw product is then cleaned in a two stage distillation.

- **Process of BASF**

O-xylene is heated up, mixed with preheated air and evaporated. This mixture is brought to a tube reactor where it is oxidised in an exothermal process on selective catalysts. The catalyst developed for the BASF process consists of a spherical carrier material, which is coated with a thin layer of TiO₂ and vanadium oxide. Other catalyst e. g. from the Wacker Company mix titanium dioxide hydrate to the coated layer to get better results. The newest developments in the catalysts techniques are annular catalysts. The lifetime of the catalyst is approximately four years. SO₂ is added if no new catalysts are used to improve the turnovers of the oxidation. The reaction heat of the exothermal reaction is used for steam generation and only partly consumed during the process. The gases, which leave the reactor, are pre-cooled and then brought to the separation system. The phthalic anhydride is condensed at ripped tube separators. The ripped tube separator is automatically cooled and heated with heat transfer oil and thus the phthalic anhydride is smelted and collected in a tank. After the separation of phthalic anhydride by-products and small amounts of phthalic anhydride remain in the exhaust gas which has to be further treated. The raw product is purified in a two staged distillation.

- **Process of Von Heyden**

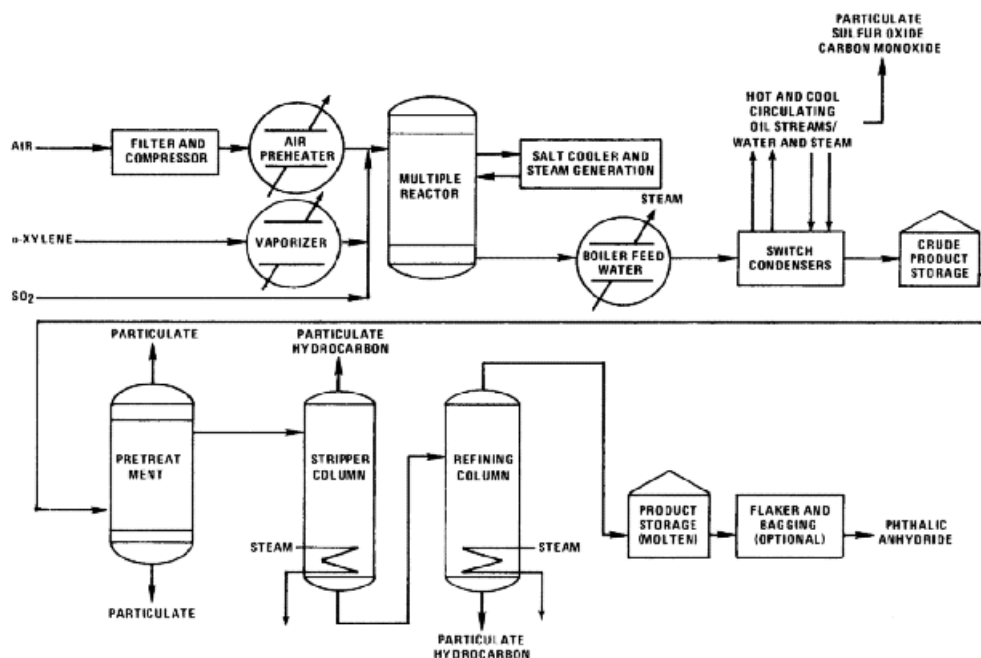
In a new development of the Von Heyden process, specially constructed tube reactors are used, which use a salt smelt for cooling, allowing an exact control of the temperature profile, and thus higher loadings of o-xylene. The constant flow of the molten salt is reached with axial flow pumps. The more intense heat generation leads to substantial energy savings.

b) Oxidation in the liquid phase

- **Process of Rhone – Progil**

Another possibility of the oxidation is the oxidation in the liquid phase. A mixture of acetic acid, o-xylene and catalyst is fed to the first reactor of a cascade. The reaction starts under pressure in the first reactor and is finished in the following reactors of the cascade. The phthalic anhydride is separated in a crystallisation unit and after pre-treatment purified in a distillation. To reach the high yields of 130 kg phthalic acid per 100 kg o-xylene the purity of o-xylene must be higher than 99 %. The industrial importance of this process is low.

In Figure 10 the general process flow for air oxidation of o-xylene to phthalic anhydride is presented.



Flow diagram for phthalic anhydride using o-xylene as basic feedstock.¹

Figure 10: Production of phthalic anhydride from o-xylene

4.5.2 Exhaust Gas Cleaning

The exhaust gas after the separation units contains high amounts of organic acids and has to be cleaned according to this. One possibility is the thermal or catalytic incineration. The other possibility is wet scrubbing with water.

The most common practice in older plants is wet scrubbing with water. The organic acids can be concentrated in the washing water and thus recovered. Using the BASF process a recovery of 5 kg maleic anhydride per 100 kg phthalic anhydride is possible. A further advantage of the recovering process of maleic anhydride is that the washing water could be re-used for exhaust gas scrubbing. Thus the PSA/MSA process works without waste water production [LENZ et al., 1989]. The disadvantage of the wet scrubbers are the high emissions of carbon monoxide, which is not washed out in the scrubber. Also aliphatic compounds are not separated in the scrubbers and stay in the exhaust gas. One by-product of the phthalic anhydride production, o-toluyaldehyde is not separated in the scrubbers, too. Small amounts of this pollutant lead to odour nuisance.

The alternative exhaust gas cleaning system is exhaust gas incineration. Thermal incineration as well as catalytic incineration are possible and made in some plants now (e. g. thermal incineration with additional natural gas in a plant in Hull). The disadvantage of thermal incineration is, that the exhaust gas with a temperature of approximately 60 °C has to be heated up to 800 °C. Another disadvantage is, that the recovery of maleic anhydride is impossible if an incinerator is used.

The most efficient system of emission control is the combined usage of a wet scrubber and catalytic incinerators. The scrubber is efficient in collecting particles and in the separation of organic acids, whereas the incinerator decreases the emissions of carbon monoxide and hydrocarbons.

4.5.3 Use of Phthalic Anhydride

The most important utilization of phthalic anhydride is the production of phthalate ester plasticizers, which are primarily used in the production of polyvinyl chloride (PVC) resins. Unsaturated polyester resins are the second largest market and the manufacture of alkyd resins is the third largest one. The remaining rest is used in smaller application, including the production of polyester polyols, dyes and pigments.

4.5.4 Austria

In Austria one plant exists using the BASF process with different catalysts and an annual production between 40 000 and 47 000 t/a. The capacity is 50 000 t/a. Between 36 000 and 44 000 tonnes o-xylene are necessary for the production of these amounts of phthalic anhydride. The main part of the plant was built in 1969 and start of production was in 1970. At the beginning of the nineties the plant was shut down and later reopened in 1995.

In the Austrian plant, first air is compressed with turbocompressors to an overpressure of 1 bar and then heated up to approximately 165 °C. O-xylene with a temperature of approximately 150 °C is injected into the hot air and evaporated. In the tube reactors (10 000 tubes with a diameter of 2.5 cm) the raw materials are oxidized over catalysts to phthalic anhydride. The load of air with o-xylene has been changed in the last years due to improved catalysts to 60 g/Nm³ compared to 40 g/Nm³ before. Newest technologies can use loadings of 100 g/Nm³ and more. The Austrian plant uses catalysts, which consist of a ceramic base material with a TiO₂ and V₂O₅ coat with different dopants. The reaction heat is removed with salt coolers and used for steam production (22 – 24 t/h). This steam is used for the generation of electricity with a steam turbine (rated power of approximately 3.5 MW). For further cooling of the reaction gas from 350 °C to 170 °C, gas coolers are used and low-pressure steam (6 bar) is produced.

For the separation of phthalic anhydride five crystallizers are used, which work at approximately 60 °C. Alternately four of them are cooled for three hours and phthalic anhydride condenses in the separators, while the fifth one is heated for 45 minutes and the solid phthalic anhydride is smelted. Different pollutants and by-products remain in the exhaust gas after the separation of phthalic anhydride. Table 40 presents the composition of the exhaust gas after the crystallizer.

Table 40: Composition of the exhaust after the crystallizer [ATMOSA Petrochemie, 1999]

component	concentration
CO	7 000 mg/Nm ³
maleic anhydride	4 000 mg/Nm ³
CO ₂	28 500 mg/Nm ³
SO ₂	~ 100 mg/Nm ³
o-xylene	30 – 40 mg/Nm ³
aliphatics	~ 30 mg/Nm ³

As mentioned before SO₂ is added, if older catalysts are used to guarantee high conversion rates of o-xylene to phthalic anhydride. Thus the amount of SO₂ in the exhaust gas strongly depends on the age of the catalysts.

For the cleaning of the exhaust gas wet scrubbers with counter current flow are used. The washing water is recirculated over a layer of Raschig rings with a height of two meters until the concentration of maleic acid reaches 250 g/l. The washing water is removed twice a day and thus between 12 000 and 13 000 t/a maleic acid solution is produced. This solution is used for the production of fumaric acid. Approximately 5.5 kg fumaric acid can be produced per 100 kg phthalic acid. After the wet scrubber the concentrations of organic anhydrides are quite low (e. g. maleic anhydride ~ 3 ppm). The most important pollutants are presented in Table 41.

Table 41: Composition of the exhaust gas (half hour mean values) after one of the wet scrubber [Niederösterreichische Umweltschutzanstalt, 1996]

time	CO	SO ₂	total carbon	CO ₂
12:00-12:30	7 100 mg/m ³	---	< 10 mg/m ³	1.23 Vol%
12:30-13:00	7 250 mg/m ³	217 mg/m ³ ²⁹	< 10 mg/m ³	1.28 Vol%
13:00-13:30	7 160 mg/m ³		< 10 mg/m ³	1.25 Vol%
13:30-14:00	7 070 mg/m ³	185 mg/m ³	< 10 mg/m ³	1.23 Vol%
14:00-14:30	7 130 mg/m ³	226 mg/m ³	< 10 mg/m ³	1.25 Vol%
14:30-15:00	7 290 mg/m ³	204 mg/m ³	< 10 mg/m ³	1.29 Vol%
mean value	7 160 mg/m³	210 mg/m³	< 10 mg/m³	1.26 Vol%

All values are related to dry exhaust gas in normal state (0 °C, 1 013 hPa). The oxygen level during the measurements differs between 16.29 and 16.36 Vol. % with a mean value of 16.33 Vol%. The volume flow of the exhaust gas was 32 278 Nm³/h related to dry exhaust gas in one of the chimneys. Also the other chimney has approximately the same volume flow. In the value of total carbon the pollutant o-toluyil aldehyde is included, which leads to odour nuisance already with small amounts.

As mentioned before alternatively to exhaust gas cleaning with only wet scrubbers, thermal or catalytic incineration for further treatment of the exhaust gas can be used. Especially the high amount of CO in the exhaust gas is reduced with this measure. Some reference plants already exist in Europe (e. g. Hull in England).

The condensed and melted phthalic anhydride of the crystallizer is purified in the further stages of the process. The first part is a stirred boiler where partly formed phthalic acid is dehydrated to phthalic anhydride. The water is removed and small amounts of KOH (~10 ppm) are added as a stabilizer. Then in a two stage distillation in the first column substances with lower boiling points (between 200 and 250 °C) are removed at the top. In the second column the pure phthalic anhydride is removed at the top. After the separation of rests of phthalic anhydride from the high boiling components of the second column, the top product of the first column (e. g. benzoic acid or maleic anhydride) and the bottom product of the second column are incinerated with additional natural gas. The heat of this incineration is used for heating the heat transfer oil, which is used for distillation. In the measurement of [Niederösterreichische Umweltschutzanstalt, 1996] only the concentration of dust was determined. The mean value was 19 mg/Nm³ related to dry exhaust gas. The mean volume flow

²⁹ hourly mean value

of the exhaust gas during the measurements was 3 405 m³/h related to moist exhaust gas at normal state. The amount of the used natural gas during the measurements was 62.5 m³/h.

Only a small part of the produced phthalic anhydride is stored in the liquid state, because high temperatures are necessary for liquid storage. If phthalic anhydride is stored or transported in the liquid state it should reach the end user in approximately two days. Due to this the main part is stored in the solid state. The solid product should be used within six months. To reduce the dust content a suction plant is used in the packaging hall. For separation of the dust bag filters are used and the separated dust is recirculated to the separation process of phthalic anhydride.

4.6 Glyoxylic – Acid and other Products of Ozonolysis

A few different processes for the production of glyoxylic acid exist:

- **Oxidation of glyoxal:** A solution of glyoxal in water is oxidized with nitric acid or with nitrogen oxides. In the first separation step oxalic acid is crystallized at temperatures of approximately 20 °C. With further cooling to temperatures between - 10 °C and 0 °C glyoxylic acid crystallises.
- **Oxidation of acetaldehyde:** During the oxidation of acetaldehyde for glyoxal production 10 % glyoxylic acid are produced. An increase in temperature and higher concentrations of nitric acid will provide higher amounts of glyoxylic acid.
- **Oxidation of ethylene:** Ethylene is oxidized with nitric acid to glyoxylic acid in the presence of palladium salt.
- **Ozonolysis of maleic anhydride:** Raw material for the production of glyoxylic acid with ozonolysis is maleic anhydride. The process uses temperatures between - 15 and - 25 °C. By-products are formic acid and carbonic acid. The advantage is that nitric acid is replaced by ozone for the oxidation and thus less emissions can be expected. The disadvantage of this process is the high amount of electric energy, which is necessary for the production of ozone.

In Austria glyoxylic acid is produced with ozonolysis and thus only this process is described in detail. The total capacity Austrian for glyoxylic acid is 14 990 t/a 50 % solution of glyoxylic acid. This production is distributed to three different plants. Two of these plants produce only glyoxylic acid, whereas the third plant is a multipurpose plant, where additionally other products (e. g. glyoxylic acid methyl ester methyl hemiacetal) are produced.

The first step in the production of glyoxylic acid is the production of dimethyl maleate from maleic anhydride and methanol. This process consists of pre-esterification, esterification, methanol distillation and neutralization.

Another part of the process is the production of ozone, which is needed in the further production steps. The ozone production consists of an ozone generator, an oxygen drier, a catalytic combustion and a pressurized scrubber.

In the next part of the process glyoxylic acid methyl ester methyl hemiacetal is produced from dimethyl maleate and ozone. Essentially the following process steps are used in this part: Ozonolysis stage 1, ozonolysis stage 2, hydrogenation, methanol distillation, two staged thin-layer evaporation and a glyoxylic acid methyl ester methyl hemiacetal (GMHA) distillation.

The last step is the production of glyoxylic acid from GMHA. The main procedure sections in this part are a saponification and an evaporation.

The exhaust gases of all three plants are incinerated in the same plant. The emissions and the emission standards of this plant are shown in Table 42. The temperature of the exhaust gas is 160 °C.

Table 42: Emissions from the exhaust gas incineration of the ozonolysis plants [DSM Fine Chemicals Austria, 1999] and [DSM Fine Chemicals Austria, 2000]

component	1998		1999		emission standard
	concentration	amount	concentration	amount	
H ₂ O	260 000 mg/Nm ³	1 788.80 t/a	260 000 mg/Nm ³	1 788.80 t/a	-
CO ₂	304 200 mg/Nm ³	2 092.90 t/a	200 000 mg/Nm ³	1 520.00 t/a	-
CO	3 mg/Nm ³	0.02 t/a	1 mg/Nm ³	0.01 t/a	50 mg/Nm ³
NO _x	121 mg/Nm ³	0.83 t/a	180 mg/Nm ³	1.37 t/a	200 mg/Nm ³
TOC	1 mg/Nm ³	0.03 t/a	1 mg/Nm ³	0.01 t/a	10 mg/Nm ³

All concentrations and emission standards are related to dry exhaust gas at 0 °C and a pressure of 1 013 mbar. The reference value for oxygen is 11 %. The following fuels are allowed to be combusted in this plant:

- Natural gas;
- Exhaust gas of the ozonolysis plants;
- Liquid by-products of the ozonolysis plants;
- Contaminated solvents of the ozonolysis plants;
- Distillation residues of the ozonolysis plants.

The halogen and sulfur content in the fuels is limited to 0.02 wt. % or 0.05 wt. % respectively. The concentration of carbon monoxide, NO_x and total organic carbon have to be measured quarterly.

Another source of emissions during the production of glyoxylic acid is the incineration of residues. Between 3 and 4 m³ natural gas and 50 and 60 kg liquid or paste like, saline organic distillation residues per hour are incinerated in the residue incineration plant. This amount of fuel leads to approximately 500 m³/h exhaust gas, which is cleaned in a scrubber. Table 43 presents the emission values and the emission standards for this incinerator.

Table 43: Emissions from residue incineration in the glyoxylic acid production [DSM Fine Chemicals Austria, 1999] and [DSM Fine Chemicals Austria, 2000]

component	1998		1999		emission standard
	concentration	amount	concentration	amount	
H ₂ O	155 000 mg/Nm ³	132.20 t/a	155 000 mg/Nm ³	130.20 t/a	-
CO ₂	183 300 mg/Nm ³	153.97 t/a	200 000 mg/Nm ³	1 080.00 t/a	-
CO	5 mg/Nm ³	0.04 t/a	1 mg/Nm ³	0.01 t/a	100 mg/Nm ³
NO _x	200 mg/Nm ³	0.19 t/a	200 mg/Nm ³	1.08 t/a	200 mg/Nm ³
TOC	<2 mg/Nm ³	0.00 t/a	1 mg/Nm ³	0.01 t/a	20 mg/Nm ³

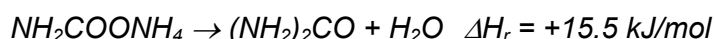
Again all concentrations and emission standards are related to dry exhaust gas at 0 °C and a pressure of 1 013 mbar. The reference value for oxygen is 11 %.

Glyoxylic acid is used for the production of vanillin, ethyl vanillin and allantoin. Other applications are the production of ion exchanger resins and as raw material in the pharmaceutical industry.

5 NITROGEN CONTAINING HYDROCARBONS

5.1 Urea

Urea is produced from NH_3 and CO_2 with the intermediate stage of ammonium carbamate. The formation of ammonium carbamate is an exothermic reaction, whereas the dehydration in the second step is endothermic. The reaction equations for the two reactions are presented below.



The turnover of the urea formation strongly depends on the reaction temperature and the NH_3/CO_2 ratio. Also the ratio of $\text{H}_2\text{O}/\text{CO}_2$ influences the yield of urea. In general the reaction conditions lead to yields between 60 and 70 % urea. An important process step is the separation of the not converted ammonium carbamate from the product and the further treatment of the separated ammonium carbamate solution.

5.1.1 Urea Production Processes

5.1.1.1 Development of Urea Production Processes

In the earliest urea production processes no recirculation of the separated off-gases was made. These processes operated with the so called “**Once Through**” principle. The off-gases were used as feedstocks for other products like ammonium nitrate, ammonium sulphate or ammonium phosphate. These processes lost their importance, because better processes have been developed.

The first step of the improvement of raw material utilization were the “**Partial Recycle Processes**”, where part of the NH_3 and CO_2 have been recovered and recycled to the process.

For further optimization of raw material utilization the so called “**Total Recycle Processes**” were developed. These processes can be divided into two groups (the stripping processes and the conventional recycle processes). The first developments involved a gas cooling and then a recombination of the gases to form a carbamate solution. In series of loops of carbamate decomposers and carbamate condensers the carbamate solution is pumped back to the reactor with a lower pressure. Improvements were achieved by the development of techniques, which decompose the carbamate without reducing the system pressure. These processes are called stripping processes and can be divided in processes using ammonia as stripping gas and processes using CO_2 for stripping.

5.1.1.2 Conventional Recycle Processes

Mitsui-Toatsu-Process: Liquid ammonia, carbamate solution and gaseous CO_2 are pressurized to 250 bar. The reaction temperature is between 195 and 200 °C. Due to the high excess of ammonia turnovers of 70 % and more related to CO_2 are reached. After the reactor the pressure of the solution is reduced to values between 60 and 80 bar in the high pressure separator and the main part of the ammonia excess is evaporated. This ammonia is freed from CO_2 and brought to an ammonia absorber where it is absorbed and condensed in cold liquid ammonia.

The solution of the high pressure separator is treated in the so called decomposers where it is freed from the carbamate due to energy input. The pressure in the decomposers is de-

creased in each step. The gas mixture (NH_3 , CO_2 and H_2O), which leaves the decomposers is subsequently condensed and solved by cooling in the absorbers. Thus a concentrated carbamate solution is produced, which is recycled to the reactor.

Montedison Process: This process works at 200 bar and 200 °C with the recirculation of carbamate solution. In the first decomposition stage at 80 bar and 190 °C a two staged condenser is used. Due to the high enthalpy of the recirculated high concentrated carbamate solution a part of the formation energy of the ammonium carbamate is removed in the condenser. In the second condenser total condensation is reached at a temperature of approximately 115 °C and thus the apparatus for the separation and re-condensation of NH_3 is not necessary.

Technip/Mavrovic heat recycle-process: This process works with recirculation of liquid carbamate. In the reactor or in the pre-reactor steam is produced due to an excess of reaction heat, which comes from an intensive heat exchange between the raw material and the hot gases of the first decomposition stage. To reach high turnovers the water content of the recirculated carbamate should be low. The process works at a temperature of 190 °C and a pressure of 250 bar.

5.1.1.3 Stripping Processes

As mentioned before the stripping processes can be divided into two groups due to the stripping agent. Several processes exist for ammonia or carbon dioxide as stripping agent. In the following section one example for each kind of stripping process is presented.

Stamicarbon-Stripping-Process: The carbamate is decomposed at reactor pressure in the stripper within this process. All of the CO_2 is added in the high pressure stripper. Due to this the partial pressure of ammonia is extremely lowered in the stripper and approximately 85 % of the carbamate is decomposed there. To remove the rest of the carbamate from the urea solution only one further decomposition stage is necessary which works at 3 – 4 bar. The heat exchanger of the second decomposition stage could be heated with the produced steam of the condenser of the stripper. The gaseous mixture of the stripper, the carbamate solution from the second decomposition stage and a part of the added ammonia are partially condensed. The heat of this condensation can be used for steam production. The produced mixture of gas and liquor is added at the bottom of the reactor with the main part of the ammonia. The reaction takes place at temperatures between 170 – 190 °C and pressures between 120 – 150 bar. The molar NH_3/CO_2 ratio is approximately 2.8.

SNAM-Progetti-Stripping-Process: The main difference to the Stamicarbon process is that ammonia is used as stripping gas instead of carbon dioxide. The process uses temperatures of approximately 185 °C and a pressure of 150 bar. The molar NH_3/CO_2 ratio is between 3.5 and 4. Part of the liquid ammonia is added to the reactor, the rest in the stripper (a film evaporator) to decompose most of the carbamate in the urea solution from the reactor. The main part of CO_2 is added to the reactor to reach the reaction temperature. Only a small part is added to the high pressure condenser.

After the reactor the solution flows to the stripper, where the carbamate is decomposed due to the gaseous ammonia, which is added. The stripper is heated with steam.

Another possibility of this process is, that the NH_3/CO_2 ratio in the reactor is increased and the ammonia excess is used for stripping. Thus no ammonia is added at the stripper, because the stripping effect is reached with the excess ammonia.

After the stripper the urea solution is freed from the rest of carbamate in conventional decomposer/absorber stages.

5.1.2 Further Treatment of the Urea Solution

The first step after the reaction and recycle part is the concentrating of the urea solution in a evaporation section to molten urea. The residence time in the evaporator must be short, because in the temperature range of the evaporator urea can be decomposed into ammonia and cyanic acid and subsequently biuret is formed. Most of the evaporation sections are two staged and operate under vacuum.

The produced urea melt can be used as raw material for different products. The other possibility is to produce a solid product. This product is either prilled or granulated. If granulation is used as solidification step normally one evaporation step is enough.

5.1.2.1 Prilling

The concentrated urea melt (99 – 99.7 %) is fed to a centrifuge the top of the prilling tower. There the urea melt forms liquid droplets, which solidify while they fall through the tower. Large volumes of cooling air are required in the prilling tower. The prilling tower is the major source of air pollution in urea production. Especially ammonia and dust (urea) are important pollutants, which are present in the exhaust gas, if no or inefficient gas cleaning systems are used. A detailed description of the prilling operation is given in Chapter 5.1.5.

5.1.2.2 Granulation

The second possibility for further treatment of urea melts to get a solid product is granulation. Most of the new plants use granulation to solidify the urea solution. The concentration of the urea feedstock may be less concentrated (> 95 %) than for prilling. Due to this lower concentration the second step of the evaporation process could be omitted. During the granulation the urea melt is sprayed onto recycled seeds or prills, which are circulated in the granulator. Simultaneously the granule size increases slowly and the melt dries. The melt deposited on the seed material is solidified by air passing through the granulator.

The advantages compared to prilling towers are that the second step of the evaporation section is not necessary and that less cooling air is needed, because the additional water of the less concentrated feedstock dissipates part of the heat, which is released during the solidification of urea.

Due to the lower amount of cooling air the cleaning of the exhaust gas is easier in the granulation process. On the one side wet scrubbing with process condensate can be used for exhaust gas cleaning. Quite high removal efficiencies for dust (urea) can be achieved by using process condensate for scrubbing, but the removal efficiency for NH_3 is not very high. For efficient NH_3 removal an acidic washing solution has to be used. The disadvantage of using acidic washing solution is that they can not be recycled to the urea production process (see also Chapter 5.1.3).

5.1.3 Gaseous and Liquid Emissions

As mentioned before the main source for gaseous emissions is the prilling or granulation system. Different exhaust gas cleaning systems exist to reduce the emissions of ammonia and urea dust, which are the main pollutants in these exhaust gases. For the prilling system dry dust collectors and electrostatic precipitators are possibilities for exhaust gas cleaning, but the most attractive abatement technique seems to be a wet scrubber. Achievable emission values for existing plants are 20 mg/Nm³ for ammonia and 20 mg/Nm³ for urea (see emission values of the Austrian plant in Chapter 5.1.5), if they use a wet scrubber for exhaust gas cleaning. A detailed description of a wet scrubber for exhaust gas cleaning of the prilling tower is given in the Chapter about the Austrian plant (see Chapter 5.1.5).

Using a granulator for solidification of the urea melt less dust is produced. The exhaust gas from the granulator is normally scrubbed with the process condensate of the urea production and recycled to the production process [EFMA, 1995]. The efficiency for NH₃ removal from the exhaust is not very high and it could be increased by using an acidic washing solution. The disadvantages of this cleaning system is that the solution could not be recycled to the urea production process. If a fertilizer production is at the same location this washing solution could be recycled in this process (see also treatment of the scrubbing solution of the prilling tower in Austria).

Another source for emissions is the concentration process of the urea solution. The condenser off-gas contains ammonia and carbon dioxide.

The main source of process water is the formation of urea, where approximately 300 kg water is produced per tonne urea. This process water contains ammonia, urea and carbon dioxide. The main part of the process water is produced in the evaporation unit and has to be treated in a special waste water treatment plant, that removes NH₃, CO₂ and urea from the process water and prepares it for discharge to running water. The recovered NH₃, CO₂ and urea are recycled into the production process.

Different waste water treatment processes exist to remove these substances from the water. Most of the processes use stripping or distillation to remove NH₃ and CO₂. To remove urea in general a hydrolyser is used. In the hydrolyser urea is decomposed into NH₃ and CO₂. These gases are discharged overhead of the hydrolyser and recycled to the production process.

5.1.4 Use of Urea

The most important use of urea is as a fertilizer. Also the use as additional substance to the fodder in agriculture gains in importance in the last years. Technically urea is used in large amounts for condensation reactions with formaldehyde for the production of resins and glues. Other applications are the production of melamine from urea and the use in the dye industry and varnish production.

5.1.5 Austria

In Austria urea is produced in one plant. The capacity of this plant is 1 400 t/d. The annual production is approximately 400 000 tonnes. In Austria the SNAM – Progetti process is used. For one tonne urea 567 kg ammonia and 735 kg CO₂ are necessary. Liquid ammonia and CO₂ react at ~ 154 bar to urea. The yield of urea is approximately 62 % and thus the rest of the carbamate solution, which is formed in the first step of the reaction from ammonia and CO₂ has to be decomposed and then recycled to the reactor. For the decomposition three thin layer evaporators are used, which work at different pressure levels. The first thin layer evaporator works at 150 bar. Subsequently the residual NH₃ and CO₂ are recovered in two following stages. The second stage works with medium pressure (~ 15 bar) and the third

stage works with low pressure (~ 5 bar). The condensation energy of the high pressure section and of the medium pressure section is recovered for steam production.

After this section the urea solution is concentrated in a two staged evaporation. Two vacuum evaporators, one with 0.4 bar and the other with 0.04 bar are used to remove water from the urea solution. 300 kg process water are produced per tonne urea. From the removed process water ammonia and urea are recovered. For urea recovery vapour washing before condensation is used. Ammonia is separated and recovered from the process water by distillation. Before the distillation of the process water the concentration of ammonia is 37 000 mg/l. With the distillation the amount of ammonia in the water is reduced to 66 mg/l. The amount of urea in the treated water is 186 mg/l and the COD value is 52 mg/l. This water is daily analysed and discharged to the running water.

After concentrating the urea solution two different possibilities exist, depending on the form of urea, which is required. For melamine production molten urea solution is needed. If solid urea is needed the Austrian plant uses a prilling tower, where the molten urea from the vacuum evaporators is solidified. First the solution is fed to rotating buckets at the top of the tower. The formed liquid droplets solidify and cool on free fall through the tower. Forced or natural up-draft of ambient air is used for cooling and drying of the liquid droplets. In Austria prior natural up-draft was enough, but since the wet scrubbers are used forced up-draft is necessary.

For cleaning of the exhaust gas of the prilling tower wet scrubbers are used. The main pollutants in the exhaust gas are dust (urea) and ammonia. Between 300 000 and 350 000 Nm³/h exhaust gas is distributed to six scrubbers. For all six scrubbers together approximately 400 m³/h circular solution and approximately 4 m³/h fresh water are necessary. The pH-value of the circular solution is 5. Table 44 presents the concentrations of ammonia and dust in the exhaust gas before and after the scrubber.

Table 44: Concentrations of ammonia and urea before and after exhaust gas cleaning of the prilling tower [AGROLINZ MELAMIN, 1999]

substance	concentration		
	before the scrubbers	after the scrubbers	emission limit values
ammonia	70 – 140 mg/Nm ³	10 – 20 mg/Nm ³	30 mg/Nm ³
dust (urea)	60 – 130 mg/Nm ³	5 – 20 mg/Nm ³	30 mg/Nm ³

The emission limits for the exhaust gas of the prilling tower are 30 mg/Nm³ for each (ammonia and urea). Between 300 and 400 l/h concentrated scrubbing solution are discharged from the scrubbers. Due to the high content of ammonium nitrate in the concentrated scrubbing solution it could not be recycled to the urea production process and is used in the fertilizer production at the same site. The concentrations of nitrogen containing components in the discharged scrubbing solution are presented in Table 45.

Table 45: Concentrations of nitrogen containing compounds in the scrubbing solution [AGROLINZ MELAMIN, 1999]

component	concentration
ammonia (calculated as N)	30 g/l
nitrate (calculated as N)	30 g/l
urea (calculated as N)	72 g/l

The investment costs for the scrubbing system have been approximately 40 million ATS. Additionally operational costs of approximately 1.5 million ATS have to be mentioned.

5.2 Melamine Production

The most important raw materials for melamine production are urea or dicyandiamide. Depending on the raw material different processes exist.

5.2.1 Production from Dicyandiamide



Controlling the temperature of this exothermal reaction ($H = -218 \text{ kJ/mole}$) is very difficult, because at temperatures higher than $350 \text{ }^\circ\text{C}$ the formed melamine is decomposed. Thus the reaction heat has to be removed from the reaction unit. Yields between 95 and 98 % are technologically possible.

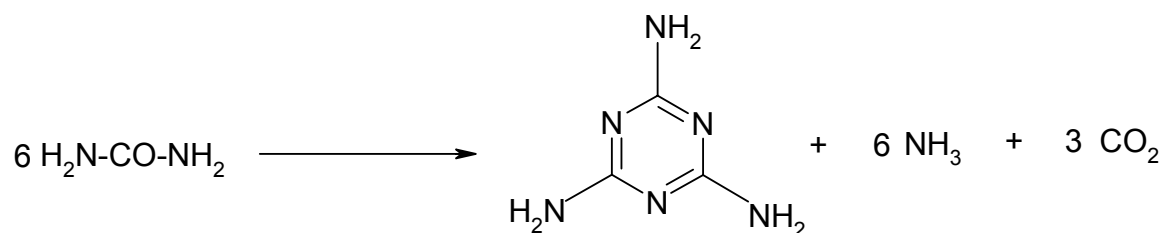
a) Processes in the liquid state

In these processes it is tried to realise the reaction in the liquid state. For this a solvent is mixed with ammonia. One example for a solvent is methanol used in the process of American Cyanamid. The disadvantage of these processes is the recovery and cleaning of the solvents. Another possibility is the production in liquid ammonia. Dicyandiamide is solved in ammonia and at approximately $160 \text{ }^\circ\text{C}$ it is converted to melamine.

b) Processes in the solid state

The main problem of these processes is the removal of the reaction heat. To avoid the formation of large amounts of by-products and to prevent the decomposition of the just formed melamine a temperature range between 300 to $330 \text{ }^\circ\text{C}$ should be established. One possibility is the addition of inert material to the dicyandiamide. Thus the value for the temperature could be reached. The process of SKW Trostberg mixes the dicyandiamide with raw melamine, which is produced in the former step.

5.2.2 Production from Urea



The production of melamine from urea is made under high pressure or on catalysts. Temperatures in all kinds of processes are higher than $360 \text{ }^\circ\text{C}$ and the yield of melamine is higher than 95 %. The reaction is highly endothermic and has a high energy consumption. Half of the urea works like a dehydration agent and is decomposed to NH_3 and CO_2 (850 kg ammonia per tonne melamine and 1 100 kg carbon dioxide per tonne melamine). The best utilization of NH_3 and CO_2 is recovery for urea production. As mentioned before the processes can be divided in high-pressure processes and catalytic processes.

5.2.2.1 High Pressure Processes

- a) **Process of Allied Chemicals:** The liquid urea is fed at the bottom of an electrically heated high-pressure reactor. Melamine is formed at 400 °C and a pressure of 130 bar. After the formation liquid melamine is removed from the reactor at the top and cooled with water in a quench tank. The melamine is solidified and forms a salt mush with the water. The cooled and dried exhaust gas is used for the recovery of ammonia.
- b) **Montecantini process:** In this process ammonia is additionally added. It works at temperatures between 380 and 400 °C and pressures between 90 and 150 bar. The reactor is heated indirectly and mechanically stirred. Normally two reactors are used. Melamine leaves the first reactor in the liquid state and is treated with pure ammonia or with the exhaust gas, which is cleaned from carbon dioxide before. This converts the by-products produced in the first reactor to melamine. After the second reactor liquid melamine forms a melamine solution with an aqueous ammonia and CO₂ solution at temperatures between 120 and 170 °C and pressures between 10 and 35 bar. This melamine solution is filtered and then melamine is crystallized.
- c) **Nissan process:** This process needs temperatures between 390 and 450 °C and a partial pressure of ammonia between 62 and 140 bar. Simultaneously with the liquid urea pre-heated ammonia gas is added at the bottom of the reactor. The reaction heat is added with an electrical heating system. Liquid melamine and the reaction gases are removed at the top of the reactor. In the next step the reaction product is moved to a separator. There solid melamine is separated at approximately 150 °C and then recrystallized.

5.2.2.2 Catalytic Low Pressure Processes

Three different processes have been established until now.

a) Process of Chemie Linz

This process works in two stages at atmospheric pressure. In the first stage urea and ammonia are added to a fluidized bed reactor with inert particles. At a temperature of 360 °C urea is decomposed to ammonia and isocyanic acid. In the second stage the reaction gases of the first stage and additional NH₃ are fed to a fixed bed reactor which contains aluminium oxide as catalyst. High condensing by-products have to be removed periodically from the catalyst (approximately every year). The temperature in this reactor is approximately 450 °C. The produced melamine vapour is quenched with water under formation of a melamine slurry. The melamine is separated by centrifugation and dried. The CO₂ in the exhaust gas is absorbed in a column with an aqueous ammonia solution. This leads to an ammonium carbonate solution, which can be used for urea production. The better solution is the separation into pure ammonia, CO₂ and water by azeotropic distillation. The separation of the decomposition of urea in the first reactor from the production of melamine in the second reactor leads to the problem that the reaction heats of the two reactors are also separated. In the first reactor of this process 3 350 kJ/kg_{urea} are consumed. This energy is provided with salt melts. In the second reactor 3 000 kJ/kg_{melamine} are produced. A great part of the heat is used for preheating NH₃.

Advantages of this process are the small attrition loss of the catalyst and that no recrystallization of the melamine is necessary. The disadvantage of this process is the bad energy performance.

b) Dutch-Staatsmijnen Process

Molten urea is injected in a fluidized bed. The bed material of this indirectly heated reactor is aluminium oxide catalyst or silica gel catalyst. The formed melamine vapour is removed from the reactor with the exhaust gas stream. In the following separation column the melamine vapour is absorbed, removed at the bottom and subsequently crystallized. The top product consists of ammonia, CO₂ and steam. For separation of the top product the gases are fed to an absorption column using liquid ammonia. The top product of this column is pure ammonia, which is recirculated to the fluidized bed reactor. The bottom product an aqueous ammonium carbamate solution is recycled to the urea production.

c) BASF process

Liquid urea is fed to a fluidized bed at approximately 370 °C. The fluidized bed contains an especially developed aluminium oxide catalyst. For the fluidizing gas exhaust gas containing NH₃ and CO₂, which is pre-heated and recirculated is used. The reaction gas after the fluidized bed reactor is cooled and filtered to remove the entrained catalyst and the by-product melem. Then the gas is cooled in a sublimation chamber to 170 – 210 °C and a fine melamine powder is produced. This powder is separated from the reaction gases in a cyclone. The exhaust gas is washed with liquid urea to separate ammonium cyanate, cyanamide and melamine and it is cooled down to 140 °C. The liquid urea is recirculated to the fluidized bed reactor. The energy demand of this process is lower than the energy demand of the other processes.

To work economically with these processes a recovery of the large amounts of CO₂ and NH₃, which are formed during the melamine formation is necessary. Again the combination with a plant for urea production seems to be the best possibility for the recovering strategy.

5.2.3 Use of Melamine

Melamine is used for the production of melamine resins, for glue production and for the production of decorative surfaces.

5.2.4 Austria

In Austria three plants for melamine production exist using the Chemie Linz process. The total capacity of these plants is 50 000 t/a. About 160 000 tonnes urea are necessary for the production of these amounts of melamine.

In the first stage liquid urea is fed into a fluidized bed reactor. There urea is decomposed into ammonia and isocyanic acid. Molten salt is used for the energy supply of this endothermic reaction. The salt melting plants for the energy supply are one source of emissions during melamine production. Each of the three melamine plants has its own plant for the energy supply, which uses natural gas as fuel. Table 46 shows the main pollutants of the three plants for energy supply. The capacities of the three melamine plants is listed additionally.

Table 46: Emissions of the energy supply plants of the three natural gas fired Austrian melamine plants [AGROLINZ, 1999]

		plant 2	plant 3	plant 4
melamine capacity		10 000 t/a	20 000 t/a	20 000 t/a
CO ₂	concentration	10 Vol. %	10 Vol. %	10 Vol. %
NO _x	concentration	348 mg/Nm ³	326 mg/Nm ³	72 mg/Nm ³

It can be seen that the salt melting plant of the newest melamine plant 4, which started with production in 1990 has the lowest NO_x emissions, due to a Low - NO_x combustor and flue gas recirculation. For the other two plants strategies for reduction of NO_x emissions are under development.

After the decomposition of urea the formation of melamine takes place in a fixed bed reactor with Al₂O₃ catalysts. After the formation the melamine vapour is quenched, centrifuged and dried. The produced by-products ammonia and CO₂ are separated in a multi-staged scrubber. Approximately 7 t/h pure ammonia from all melamine plants are recycled to the ammonia storage facilities. Pure CO₂ is removed by azeotropic distillation from ammonium carbonate solutions. Only part of the produced CO₂ (maximum 4 500 kg/h) is needed for urea production and thus recycled. The rest is disposed of. Table 47 shows the CO₂ emissions of the three melamine plants in 1996.

Table 47: CO₂ emissions of the three CO₂ strippers in the melamine plants [AGROLINZ, 1997]

		melamine plant 2	melamine plant 3	melamine plant 4
CO ₂	concentration	99.9 %	99.9 %	99.9 %
	amount	10 148.7 t/a	18 590 t/a	19 066.15 t/a

The three plants have a central exhaust gas scrubber. In sum approximately 8 000 Nm³/h exhaust gas is treated. The scrubber is a counter current flow scrubber with two stages. In the first section, part of the ammonia is absorbed and most of the water in the exhaust gas is condensed. In the second stage the main part of ammonia is absorbed. The washing water is recirculated to a desorption unit, where the ammonia is separated from the washing water and recycled to the melamine plant. For better energy performance several heat exchangers are included in the washing/desorption system. Before the exhaust gas is cleaned the concentration of ammonia, the main pollutant in the exhaust gas is ~25 000 mg/Nm³. After the scrubber the ammonia concentration is less than the emission limit of 30 mg/Nm³ (mean concentration in 1996 5.5 mg/Nm³). In 1996 the total annual ammonia emissions of the three plants in the exhaust gas was 346 kg. Due to the fact that the washing water is recirculated, only a small amount of washing water has to be added to the washing cycle. The investment costs for this scrubbing system, including costs for the desorption unit and heat exchangers have been approximately 5 Mio. ATS. The costs for the column, which is used for the scrubber are not included in the 5 Mio. ATS.

As mentioned before a waste water treatment plant for the waste water of the three melamine plants is in use since August 1999. For the treatment a thermal hydrolysis reactor is used to decompose several impurities, by-products and melamine in the waste water to NH₃ and CO₂. Subsequently ammonia and CO₂ are separated by distillation and recycled to the NH₃/CO₂ separation section of the process. The remaining waste water (approximately 200 m³/d) is fed to the cooling water return of the Chemie Park Linz. The cooling water return is directly discharged to the running water without any treatment in a sewage treatment plant.

6 GENERIC BAT

Based on the experience of Austrian plants as described in the Chapters above and on a comparison of literature the techniques given in Table 48 can be seen as BAT in the Large Volume Organic Chemical Industry. Also associated emission values and reduction efficiencies are included in this Table. The mentioned techniques are divided into 8 groups, dependent on the type of pollutant, which has to be separated or abated:

- Recovery and/or abatement of VOC;
- Abatement of particulates;
- Abatement of Odour;
- Abatement of SO₂ and acid gases;
- Abatement of NO_x;
- Abatement of dioxins;
- Abatement of mercury;
- Abatement of ammonia and amines;
- Abatement of hydrogen sulphide.

Table 48: BAT and associated emission values for the production of Large Volume Organic Chemicals³⁰

	Technology	BAT Values	References	Remark
Recovery / Abatement of VOC	Selective Membrane Separation	90 – > 99 % [CONCAWE, 2000] 99 – 99.9 % Recovery [INFOMIL, 1999]	[1. Draft BRef WW & WGT, 2000a] [1. Draft BRef Refineries, 2000]	Indicative application range 1 – > 10 gvoc/m ³
	Condensation	Condensation: 50 – 98 % [UK EA, 1999] + additional abatement [UK EA, 1999] Cryo-condensation: 95 - 99 % [UK EA, 1999] 99.8 – 99.95 % Recovery [INFOMIL, 1999]	[1. Draft BRef LVOc, 2000a] [1. Draft BRef WW & WGT, 2000a] [1. Draft BRef Refineries, 2000]	Indicative application range for condensation: flow 100 – > 100 000 m ³ /h 50 – > 100 gvoc/m ³ for cryo-condensation: flow 10 – 1000 m ³ /h 20 – 100 gvoc/m ³ 20 mbar – 6 bar
	Adsorption	95 – 99 % [UK EA, 1999] ³¹ 99.95 – 99.99 % Recovery [INFOMIL, 1999]	[1. Draft BRef LVOc, 2000a] [1. Draft BRef Refineries, 2000] [1. Draft BRef WW & WGT, 2000a]	Indicative application range for regenerative adsorption flow 100 – > 100 000 m ³ /h 0.01 – 10 gvoc/m ³ , 1 – 20 atm non regenerative adsorption flow 10 – > 1000 m ³ /h 0.01 – 1.2 gvoc/m ³
Abatement of VOC	Scrubbers	95 – 98 % Reduction [UK EA, 1999] 99 – 99.95 % Reduction [INFOMIL, 1999]	[1. Draft BRef LVOc, 2000a] [1. Draft BRef Refineries, 2000] [UBA, 2000a]	Indicative application range flow 10 – 50 000 m ³ /h 0.3 – > 5 gvoc/m ³

³⁰ If nothing else is stated all BAT concentrations are related to standard conditions (dry exhaust gas, 0 °C and 101.3 kPa) and an oxygen content of 3 Vol. %, half hourly

³¹ for non regenerative adsorption 90 – 99 %

	Technology	BAT Values	References	Remark
Abatement of VOC	Thermal Incineration	99 % Reduction [UK EA, 1999] 99.8 – 99.99 % Reduction [INFOMIL, 1999] VOC ³² < 1 – 20 mg/m ³	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000]	Indicative Application range flow 1000 – 100 000 m ³ /h 0.2 - > 10 g _{VOC} /m ³ The proposed level of 1 – 20 mg/m ³ is based on emission limits and measured values of 5 Austrian plants from 3 different branches of LVOC ³³
	Catalytic Incineration	99 % Reduction [UK EA, 1999] 95 – 99 % Reduction [INFOMIL, 1999] VOC ³² < 1 – 20 mg/m ³	[1. Draft BRef LVOC, 2000a] [1. Draft BRef Refineries, 2000] [1. Draft BRef WW & WGT, 2000a]	Indicative application range flow 10 – 100 000 m ³ /h 0.05 – 3 g _{VOC} /m ³
	Flaring	elevated flares > 99 % ground flares > 99.5 %	[UBA, 2000a] [1. Draft BRef WW & WGT, 2000b]	
	Cyclone	< 95 % Reduction ³⁴	[1. Draft BRef WW & WGT, 2000c]	Cyclones are only seen as BAT in combination with an other abatement techniques
	ESP ³⁵	5 – 15 mg/Nm ³ 99 – 99.9 % reduction	[1. Draft BRef Refineries, 2000] [UBA, 2000b]	
Abatement of Particu- lates	Fabric Filter ³⁵	< 5 mg/Nm ³	[1. Draft BRef Refineries, 2000] [UBA, 2000b]	

³² The reduction efficiency of regenerative or recuperative incinerators may be lower than 99 %, but the suggested BAT value of < 20 mg/Nm³ can be achieved with these technologies.

³³ Included in the different branches are the production of formaldehyde, maleic anhydride and glyoxylic acid.

³⁴ Strongly dependant on the particle size

³⁵ There are a lot of examples that ESPs and Fabric filters can reach the values given above from different industrial branches. For examples see the BRef on “Non Ferrous Metals”.

	Technology	BAT Values	References	Remark
Abatement of Particulates	Two stage dust filter	~ 1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000d]	
	Ceramic filter	< 1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000e]	
	Absolute Filter	< 0.1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000f]	
	HEAF Filter	droplets up to 99 % aerosols up to 99 %	[1. Draft BRef WW & WGT, 2000g]	
	Mist Filter	dust up to 99 % aerosols up to 99 %	[1. Draft BRef WW & WGT, 2000h]	
	Adsorption	80 – 95 % Reduction for odour	[1. Draft BRef WW & WGT, 2000i]	Indicative application range 10 000 – 200 000 ou/Nm ³
Odour	Biofilter	75 – 95 % Reduction for odour ³⁶	[1. Draft BRef WW & WGT, 2000j]	Indicative application range 20 000 – 200 000 ou/Nm ³
	Wet limestone scrubbing	90 – 97 % Reduction SO ₂ < 100 mg/Nm ³	[BRef Cement & Lime, 2000] [BRef Glass, 2000]	
Abatement of SO ₂ and acid gases	Scrubbers	HCl ³⁷ < 10 mg/Nm ³ HBr ³⁷ < 5 mg/Nm ³ HF < 1 mg/Nm ³	Permits of Austrian plants [1. Draft BRef WW & WGT, 2000k] [BRef Cement & Lime, 2000] [BRef Glass, 2000]	alkaline scrubbers

³⁶ with a load of > 5 000 ou/Nm³

³⁷ Concentrations are based on current permits of Austrian organic chemical plants (daily mean value at standard conditions; the half hourly values are HCl < 30 mg/m³ and HBr < 10 mg/m³)

	Technology	BAT Values	References	Remark
Abatement of SO ₂ and acid gases	Semi Dry Sorbent Injection	SO ₂ < 100 mg/Nm ³ HCl < 10 mg/Nm ³ HF < 1 mg/Nm ³	[1. Draft BRef WW & WGT, 2000] [BRef Cement & Lime, 2000] [BRef Glass, 2000]	
Abatement of NO _x	SNCR	50 – 80 % NO _x reduction	[1. Draft BRef WW & WGT, 2000m] [BRef Cement & Lime, 2000] [BRef Glass, 2000]	
	SCR	85 to 95 % reduction NO _x < 50 mg/m ³ NH ₃ < 5 mg/m ³	The achievable emission concentration are based on values given in [1. Draft BRef LVOC, 2000b]	
Dioxins	Primary measures + Adsorption	< 0.1 ng TEQ/Nm ³	[UBA, 2000c]	generation of dioxins should be avoided as far as possible
Mercury	Adsorption	0.05 mg/Nm ³	[1. Draft BRef WW & WGT, 2000j]	< 0.01 mg/Nm ³ measured at Austrian waste incineration plants
Ammonia ³⁸ and amines	Scrubber	< 1 – 10 mg/Nm ³	[1. Draft BRef WW & WGT, 2000k]	Acid scrubber
H ₂ S	Adsorption	80 – 95 % reduction 1 – 5 mg/Nm ³	[1. Draft BRef WW & WGT, 2000j] Permit of Austrian plant	

³⁸ Melamin plant in Austria is permitted for 30 mg NH₃/Nm³ half hour mean value, achieving about 6 mg/Nm³ yearly average, raw gas: 25 000 mg NH₃/Nm³, 8000 Nm³/h

7 LEGISLATION

7.1 Air

In Austria no special legislation concerning emission standards for air emissions of the chemical industry do exist. In general the “Gewerbeordnung” (BGBl. 1994/194 i.d.F. BGBl. 2000/121) regulates the licensing of chemical plants. Plants have to use the state of art in their performance due to the “Gewerbeordnung”. Emission standards for air emissions from chemical plants are usually based on the German “Technical Instructions on Air Quality” (TA – Luft, 1986).

Combustion plants are regulated with the “Feuerungsanlagenverordnung” (BGBl. II 1997/331). Not included in this ordinance are steam boilers inclusive waste heat boilers, the afterburning of exhaust gases, gas turbines and combustion engines.

Emission standards for boiler plants are regulated by the “Luftreinhaltegesetz für Kesselanlagen” (BGBl. 1988/380 i.d.F. BGBl. I 1998/158) and the “Luftreinhalteverordnung für Kesselanlagen” (BGBl. 1989/19 i.d.F. BGBl. II 1997/324).

7.1.1 Feuerungsanlagenverordnung (Ordinance for Firing Installations) (BGBl. II 1997/331)

The “Feuerungsanlagenverordnung” regulates emissions of combustion plants with a nominal thermal output of 50 kW or more. This ordinance is based on § 82 Abs. 1 of the “Gewerbeordnung”. As mentioned before steam boilers inclusive waste heat boilers, afterburning of exhaust gases, gas turbines, combustion engines and plants using waste as fuel are not regulated with this ordinance.

The “Feuerungsanlagenverordnung” provides different emission standards, depending on the used fuel and on the thermal output. The emission standards for coal and coke firing plants, for oil-fired furnaces and combustion plants for gaseous fuels are presented in the following.

a) Coal and coke firing plants

Table 49: Emission standards for furnaces using coal or coke [BGBl. II 1997/331]

pollutant		capacity ³⁹ [MW]					
		≤ 0.35	> 0.35 - 1	> 1 – 2	> 2 – 10	> 10 - 50	> 50
Dust	mg/m ³	150	150	150	50	50	50
SO ₂	mg/m ³	–	–	–	–	400	200
CO	mg/m ³	1 000	1 000	150	150	150	150
NO _x	mg/m ³	–	400	400	400	350	100

The emission standards are related to dry exhaust gas at 0 °C, a pressure of 1 013 hPa and an oxygen content of 6 % in the exhaust gas.

³⁹ The capacity is defined as the average of the hourly added amount of heat related to the calorific value of the fuel.

b) Oil firing plants

In Austria four different kinds of heating oils exist. The sulphur content in the different kinds of heating oil is laid down in the Verordnung über den Schwefelgehalt von Heizölen (BGBl. 1989/94 i.d.F. BGBl. 1994/545). Table 50 presents the maximum sulphur content in different kinds of heating oil in Austria.

Table 50: Maximum sulphur content of different kinds of heating oil [BGBl. 1994/545]

kind of heating oil	sulphur content
heating oil extra light	0.10 mass %
heating oil light	0.20 mass %
heating oil medium	0.60 mass %
heavy fuel	1.00 mass %

For the lowest capacities of firing installations the quality of heating oils to be used there, is restricted (Table 51) in the “Ordinance for Firing Installations”. Heating oils with a higher sulphur content may be used in an installation with a lower power stage if equal SO₂ emission levels to fuel in Table 51 are guaranteed by other measures.

Table 51: Power stages for the use of different kinds of heating oils [BGBl. II 1997/331]

capacity ³⁹	heating oil
≤ 0.07 MW	extra light
> 0.07 – 5 MW	extra light light
5 – 10 MW	extra light light medium
> 10 MW	all kinds of heating oils

Some of the emission standards are different for the different kinds of heating oils. The following four Tables present the emission standards for dust, SO₂, CO and NO_x in oil firing plants.

Table 52: Emission standards for dust using heating oils as fuel [BGBl. II 1997/331]

fuel	capacity ³⁹		
	> 2 – 30 MW	> 30 – 50 MW	> 50 MW
heating oil extra light	30 mg/m ³	30 mg/m ³	30 mg/m ³
heating oil light	50 mg/m ³	35 mg/m ³	35 mg/m ³
heating oil medium	60 mg/m ³	50 mg/m ³	35 mg/m ³
heavy fuel	60 mg/m ³	50 mg/m ³	35 mg/m ³

The emission standards for SO₂ and CO are related to the thermal output of the firing plants.

Table 53: Emission standards for SO₂ using heating oils as fuel [BGBl. II 1997/331]

pollutant	capacity ³⁹	
	> 50 – 300 MW	> 300 MW
SO ₂	350 mg/m ³	200 mg/m ³

Table 54: Emission standards for CO using heating oils as fuel [BGBl. II 1997/331]

pollutant	capacity ³⁹	
	≤ 1 MW	> 1 MW
CO	100 mg/m ³	80 mg/m ³

For NO_x different emission standards for different kinds of heating oils are distinguished. Again the thermal output is an other criterion for the emission standard. Table 55 shows the different emission standards for NO_x.

Table 55: Emission standards for NO_x using heating oils as fuel [BGBl. II 1997/331]

Fuel	capacity ³⁹			
	≤ 3 MW	> 3 – 10 MW	> 10 – 50 MW	> 50 MW
heating oil extra light	150 mg/m ³	150 mg/m ³	150 mg/m ³	100 mg/m ³
heating oil light	450 mg/m ³	400 mg/m ³	350 mg/m ³	100 mg/m ³
heating oil medium	450 mg/m ³	450 mg/m ³	350 mg/m ³	100 mg/m ³
heavy fuel	450 mg/m ³	450 mg/m ³	350 mg/m ³	100 mg/m ³

The emission standards for liquid fuels are related to dry exhaust gas at 0 °C, a pressure of 1 013 hPa and an oxygen content of 3 % in the exhaust gas.

c) Plants using gaseous fuels

For firing plants using gaseous fuels (natural gas or liquefied petroleum gas) the “Feuerungsanlagenverordnung” provides only emission standards for NO_x and CO. Table 56 presents these emission standards.

Table 56: Emissions standards for gaseous fuels [BGBl. II 1997/331]

pollutant	fuel	capacity ³⁹	
		≤ 3 MW	> 3 MW
CO	natural gas	80 mg/m ³	80 mg/m ³
	liquefied petroleum gas	80 mg/m ³	80 mg/m ³
NO _x	natural gas	120 mg/m ³	100 mg/m ³
	liquefied petroleum gas	160 mg/m ³	130 mg/m ³

The emission standards are related to dry exhaust gas at 0 °C, a pressure of 1 013 hPa and an oxygen content of 3 %. For firing places with high temperature processes higher NO_x

emissions are allowed. Using natural gas 200 mg/m³ NO_x and using liquefied petroleum gas at maximum 260 mg/m³ NO_x are allowed.

The limits for continuous measurements of different pollutants depend on the kind of fuel, which is used and on the capacity³⁹ of the plant. Table 57 presents these values.

Table 57: Capacity³⁹, which requires a continuous measurement of the pollutant [BGBl. II 1997/331]

fuel	pollutant			
	dust	CO	SO ₂	NO _x
solid	> 10 MW	> 10 MW	> 30 MW	> 30 MW
liquid	> 10 MW	> 10 MW	> 50 MW	> 30 MW
gaseous	–	> 10 MW	–	> 30 MW

This ordinance came into force on 1.6.1998. Firing plants, which have been approved before this date have to comply with the emission values of this ordinance within five years, or if they do exceed these values no more than 50 % they have to keep the emission limits eight years later.

7.1.2 Luftreinhaltegesetz and Luftreinhalteverordnung für Kesselanlagen (Clean Air Act and Clean Air Ordinance for Steam Boilers) (LRG-K and LRV-K)

In Austria emissions of steam boiler plants and waste heat boilers are regulated by the “Luftreinhaltegesetz für Kesselanlagen” (BGBl. 1988/380 i.d.F. BGBl. I 1998/158) and the ordinance “Luftreinhalteverordnung für Kesselanlagen” (BGBl. 1989/19 i.d.F. BGBl. II 1997/324). The emission standards for dust, SO₂, CO and NO_x due to the Luftreinhalteverordnung für Kesselanlagen are presented in the following Tables. They depend on the kind of fuel and on the thermal output of the plants.

Table 58: Emission standards for dust [LRV-K, BGBl. 1989/19 i.d.F. BGBl. II 1997/324]

fuel	capacity ³⁹			
	< 2 MW	2 – 30 MW	30 – 50 MW	> 50 MW
solid fuels ⁴⁰	150 mg/m ³	50 mg/m ³		
gaseous fuels	–	5 mg/m ³	5 mg/m ³	5 mg/m ³
heating oil extra light	–	30 mg/m ³	30 mg/m ³	30 mg/m ³
heating oil light	–	50 mg/m ³	35 mg/m ³	35 mg/m ³
heating oil medium	–	60 mg/m ³	50 mg/m ³	35 mg/m ³
heavy fuel	–	60 mg/m ³	50 mg/m ³	35 mg/m ³

⁴⁰ wood is excluded

Table 59: Emission standards for SO₂ [LRV-K, BGBl. 1989/19 i.d.F. BGBl. II 1997/324]

fuel	capacity ³⁹		
	10 – 50 MW	50 – 300 MW	> 300 MW
brown coal	400 mg/m ³	400 mg/m ³	400 mg/m ³
other solid fuels ⁴⁰	400 mg/m ³	200 mg/m ³	200 mg/m ³
liquid fuels	1 700 mg/m ³	350 mg/m ³	200 mg/m ³

Table 60: Emission standards for CO [LRV-K, BGBl. 1989/19 i.d.F. BGBl. II 1997/324]

fuel	capacity ³⁹	
	≤ 1 MW	> 1 MW
solid fuels	1 000 mg/m ³	150 mg/m ³
liquid fuels	100 mg/m ³	80 mg/m ³
liquefied petroleum gas	100 mg/m ³	
natural gas	80 mg/m ³	

Table 61: Emission standards for NO_x [LRV-K, BGBl. 1989/19 i.d.F. BGBl. II 1997/324]

fuel	capacity ³⁹			
	0.35 – 3 MW	3 – 10 MW	10 – 50 MW	> 50 MW
solid fuels	400 mg/m ³		350 mg/m ³	200 mg/m ³
gaseous fuels	125 mg/m ³	100 mg/m ³		
heating oil extra light	150 mg/m ³			
heating oil light	450 mg/m ³ ⁴¹	400 mg/m ³	350 mg/m ³	100 mg/m ³
heating oil medium	450 mg/m ³		350 mg/m ³	100 mg/m ³
heavy fuel	450 mg/m ³		350 mg/m ³	100 mg/m ³

The emission standards for solid fuels are related to 6 % oxygen in the exhaust gas. For liquid and gaseous fuels they are related to 3 % oxygen. All emission values are related to dry exhaust gas at 0 °C and a pressure of 1 013 mbar.

7.1.3 Technical Instructions on Air Quality (TA – Luft, 1986)

The basic law for air pollution control and noise abatement in Germany is the Federal Immission Control Act (Bundes-Immissionsschutzgesetz, BImSchG). It primarily aims towards the protection of the medium air, but it also applies to the media water and land in the case pollution is introduced via the air. The BImSchG is complemented by ordinances and the Technical Instructions on Air Quality (TA – Luft, 1986). Especially the TA – Luft specifies in more detail requirements to be met by installations that are subject of licensing.

The Technical Instructions on Air Quality (TA – Luft, 1986) have been set up as general administrative regulations related to § 48 BImSchG. It serves to protect the public and the

⁴¹ from 1.1.2001 400 mg/m³

neighbourhood against damaging nuisance due to air pollution and for precaution against harmful nuisance due to air pollution.

The TA – Luft puts the demands, which have to be made during the permit procedure of industrial or commercial plants in a concrete form. The authorities have to bring the TA – Luft into effect during the approval procedure with an administration act. On the basis of emission standards and other demands of the TA – Luft the authorities lay down emission standards in the decision of the permit.

The TA – Luft regulates:

- the principles for the approval for construction and operation of installations;
- the determination and valuation of immissions;
- the limitation of emissions;
- the redevelopment of existing installations.

The prior aim of the evaluation of immissions is the protection against concrete dangers due to immissions. The prior aim of the limitation of emissions is precaution. These priorities are based on the knowledge that air pollution could frequently not be assigned to an individual polluter. Where the assignment to an individual polluter is impossible, precaution measures have to be made to prevent potential dangers.

One basic idea of the TA – Luft is that precaution measures have to be stricter for pollutants with a higher risk potential. Unhealthy properties (e. g. carcinogenic, teratogenic and acute or chronically toxicity), effects on the environment (plants, animals, ecosystems), the behaviour in the environment (persistence and accumulation) and the amount of the emitted substance have to be considered in the valuation of substances.

In Austria the TA – Luft is used as a guideline by the permitting authorities for substances where no Austrian regulations do exist. The following Chapter deals with emission standards of the TA – Luft.

Emission standards in the TA – Luft:

In the TA – Luft general emission standards for different groups of pollutants are summarised. One group are **carcinogenic substances** (Chapter 2.3), which are divided into three different classes according to their hazard. For dust, emission standards for **total dust** (Chapter 3.1.3) emissions and for **dustlike inorganic substances** (Chapter 3.1.4), which are again divided into three classes, are provided in the TA – Luft. **Vaporous or gaseous inorganic substances** (Chapter 3.1.6) are divided into four different classes with different emission standards. Different **organic substances** are listed in Annex E of the TA – Luft. Again they are classified according to their dangerousness in three different classes with different emission standards.

All general emission standards of the TA – Luft are maximum emission values and related to exhaust gas at 0 °C and a pressure of 1 013 mbar. Additionally the mass flow of the pollutant groups has to be considered for the approval. Thresholds of the pollutant groups are defined in the TA – Luft. Above these mass flows the emission limits of the TA – Luft should be applied. Below these mass flows emission limits of the TA – Luft should not be exceeded significantly.

Additionally to the general emission standards, special standards for certain kinds of plants do exist. They are listed in Chapter 3.3 of the TA – Luft. In the following Chapters the emission standards for the different groups of pollutants and special emission standards for plants of the organic chemistry are summarised.

Since the TA – Luft was enacted in 1986, local authorities sometimes demand stricter emission limit values.

Organic substances:

Also for organic compounds maximal emission values do exist (Chapter 3.1.7 of the TA – Luft). They are divided into three different classes, depending on the hazard of the different substances. Substances of class 1, the most dangerous class, are limited with 20 mg/m³. The maximum emission values for class two and three are 100 mg/m³ and 150 mg/m³. The allocation of substances to the different classes is made in Annex E of the TA-Luft. Table 62 presents examples of substances from the different classes. Substances, which are not listed in Annex E, should be allocated to the same class as the substance, which has the most similar effect on the environment.

Table 62: Examples for emission limits for organic substances [TA – Luft, 1986]

Substances		
Class 1	Class 2	Class 3
mass flow ≥ 0.1 kg/h	mass flow ≥ 2 kg/h	mass flow ≥ 3 kg/h
acetaldehyde	acetic acid	acetone
aniline	butyraldehyde	2-butanone
chloroform	carbon disulphide	dibutylether
1,2 dichloroethane	chlorobenzene	dichloromethane
diethylamine	cyclohexanone	dimethylether
ethylamine	dimethyl formamide	ethyl acetate
formaldehyde	ethyl benzene	ethanol
formic acid	propionic acid	N-methylpyrrolidone
maleic anhydride	toluene	olefins (except 1,3-butadiene)
methyl chloride	ethylene glycol	paraffins (except methane)
phenol	xylene	trichlorofluoromethane
Σ 20 mg/m ³	Σ 100 mg/m ³	Σ 150 mg/m ³

The above mentioned substances are only a part of the substances, which are listed in Annex E of the TA-Luft. For substances with strong effects on the environment (e. g. PCDD/F or PCB) stricter emission standards than for class I substances have to be prescribed. The emissions of these substances have to be reduced as much as possible taking into consideration the appropriateness of means (Verhältnismäßigkeitsprinzip). For example the 17. BImSchV limits the emissions of dioxins with 0.1 ng TEQ/m³.

Carcinogenic substances:

Emission standards for carcinogenic substances are listed in Chapter 2.3 of the TA – Luft. The emissions of carcinogenic substances have to be reduced as much as possible taking again into consideration the appropriateness of means (Verhältnismäßigkeitsprinzip). This minimisation rule goes beyond the maximum emission values, which are presented in Table 63.

Table 63 presents the maximum values for the emissions of carcinogenic substances, if the minimum mass flows for these substances are exceeded. As mentioned before they are divided into three different classes.

Table 63: Maximal emission values for carcinogenic substances [TA-Luft, 1986]

Substances	maximum emission value
class 1 (mass flow ≥ 0.5 g/h)	
asbestos as fine dust	
benzopyrene	
beryllium and its compounds in respirable forms	
dibenzoanthracene	
2-naphthylamine	
sum of class 1 substances	0.1 mg/m³
class 2 (minimum mass flow ≥ 5 g/h)	
arsenic trioxide, arsenic pentoxide, arsenious acid and its salts and arsenic acid and its salts (in respirable form)	
chromium(VI)compounds (in respirable form), calcium chromate, strontium chromate, zinc chromate and chromium(III)chromate	
cobalt (in the form of respirable dusts/aerosols of cobalt metal in hardly soluble cobalt salts)	
3,3-dichlorobenzidine	
dimethylsulphate	
ethylene imine	
nickel (in the form of respirable dust/aerosols of metallic nickel, nickel sulfide, nickel oxide, nickel carbonate and nickel tetracarbonyl)	
sum of class 2 substances	1 mg/m³
class 3 (minimum mass flow = 25 g/h)	
acrylonitrile	
benzene	
1,3 butadiene	
epichlorhydrine	
1,2 dibromoethane	
ethylene oxide	
propylene oxide	
hydrazine	
vinyl chloride	
sum of class 3 substances	5 mg/m³

Dust and dustlike inorganic substances:

Table 64 presents the maximum emission values for dust. On the one side the total emissions of dust (Chapter 3.1.3 of the TA – Luft) are limited with an emission standard of 50 mg/m³ if a mass flow of 0.5 kg/h is exceeded. For mass flows lower than 0.5 kg/h the emission standard for total dust emissions is 150 mg/m³. On the other side lower emission values for special inorganic dustlike substances (Chapter 3.1.4 of the TA – Luft) are specified. These substances are divided into three classes according to their hazard.

Table 64: Emission values for dust and dustlike inorganic substances [TA-Luft, 1986]

substances	maximum emission value
total dust	
mass flow ≤ 0.5 kg/h	150 mg/m ³
mass flow > 0.5 kg/h	50 mg/m ³
inorganic substances in the form of dust:	
class 1 (mass flow ≥ 1 g/h)	
cadmium and its compounds (calculated as Cd)	
mercury and its compounds (calculated as Hg)	
thallium and its compounds (calculated as Tl)	
sum of class 1 substances	0.2 mg/m³
class 2 (mass flow ≥ 5 g/h)	
arsenic and its compounds (calculated as As)	
cobalt and its compounds (calculated as Co)	
nickel and its compounds (calculated as Ni)	
selenium and its compounds (calculated as Se)	
tellurium and its compounds (calculated as Te)	
sum of class 2 substances	1 mg/m³
class 3 (mass flow ≥ 25 g/h)	
antimony and its compounds (calculated as Sb)	
lead and its compounds (calculated as Pb)	
chromium and its compounds (calculated as Cr)	
cyanides easily soluble (e.g. NaCN calculated as CN)	
fluorides easily soluble (e.g. NaF calculated as F)	
copper and its compounds (calculated as Cu)	
manganese and its compounds (calculated as Mn)	
platinum and its compounds (calculated as Pt)	
palladium and its compounds (calculated as Pd)	
rhodium and its compounds (calculated as Rh)	
vanadium and its compounds (calculated as V)	
tin and its compounds (calculated as Sn)	
sum of class 3 substances	5 mg/m³

Dustlike inorganic substances with the suspect of carcinogenic potential are assigned to class 3. Thus the emission standard for the sum of these substances is 5 mg/m³.

Vaporous and gaseous inorganic substances:

In Chapter 3.1.6 of the TA – Luft the emission standards for vaporous and gaseous inorganic substances are limited. Table 65 presents these emission limits. As mentioned before the different pollutants of this group are divided into four classes with different emission limits.

Table 65: Maximum emission values for vaporous or gaseous inorganic substances [TA-Luft, 1986]

substance	maximum emission value
class 1 (mass flow ≥ 10 g/h)	
arsine	1 mg/m ³
cyanogen chloride	1 mg/m ³
phosgene	1 mg/m ³
hydrogen phosphide	1 mg/m ³
class 2 (mass flow ≥ 50 g/h)	
bromine and its vaporous or gaseous compounds (calculated as hydrogen bromide)	5 mg/m ³
chlorine	5 mg/m ³
hydrogen cyanide	5 mg/m ³
fluorine and its vaporous or gaseous compounds (calculated as hydrogen fluoride)	5 mg/m ³
hydrogen sulphide	5 mg/m ³
class 3 (mass flow ≥ 0.3 kg/h)	
vaporous or gaseous inorganic chlorine compounds (if not allocated to class 1) (calculated as hydrogen chloride)	30 mg/m ³
class 4 (minimum mass flow = 5 kg/h)	
sulphur oxides (SO ₂ and SO ₃) calculated as SO ₂	500 mg/m ³
nitrogen oxides (NO and NO ₂) calculated as NO ₂	500 mg/m ³

Diffuse emissions:

Requirements for the control of diffuse emissions from the storage, processing and conveying of dust producing goods are laid down in Chapter 3.1.5 and for liquid organic substances in Chapter 3.1.8 of the TA Luft. Mainly special mechanical devices for the construction type of the storage facilities or the pumps, compressors, flanged joints or valves when conveying liquids are required.

Emission standards for the production of organic chemicals:

Additionally to the above mentioned general emission standards, a few special requirements for plants of the chemical industry exist in the TA – Luft. For some production processes

special emission limit and/or the kind of the exhaust gas cleaning, which must be used are provided by the TA – Luft. Some examples for plants producing organic chemicals are mentioned below. Also special measures and/or regulations for existing plant for maleic anhydride and ethyl benzene production, for plants for FCHCs are listed in the TA – Luft. For the production of hydrocarbons the special measures for refineries have to be considered.

Production of acrylonitrile:

For the production of acrylonitrile the emissions of the reaction system and of the absorber have to be incinerated. The concentration of acrylonitrile in the exhaust gas of the incinerator has to be lower than 0.2 mg/m³.

Production of dichloroethane or vinyl chloride:

In 1,2-dichloroethane or vinyl chloride production plants the exhaust gas has to be treated in an exhaust gas cleaning system and the concentrations of vinyl chloride and 1,2-dichloroethane in the exhaust gas have to be lower than 5 mg/m³.

Continuous measurement of pollutants:

For some kinds of plants the TA-Luft gives some guidances about the measurement of different pollutants. For dustlike, gaseous and vaporous emissions mass flows are specified, above which a continuous measurement of pollutants is required. The relevant gaseous and vaporous substances are presented in Table 66.

Table 66: Thresholds (mass flow) for continuous measurements [TA – Luft, 1986]

component	mass flow
sulphur dioxide	50 kg/h
nitric oxide and nitrogen dioxide (calculated as nitrogen dioxide)	30 kg/h
carbon monoxide (if it is used to assess the completeness of combustion)	5 kg/h
carbon monoxide (in all other cases)	100 kg/h
fluorine and its gaseous compounds (calculated as hydrogen fluoride)	0.5 kg/h
gaseous inorganic chlorine compounds (calculated as hydrogen chloride)	3 kg/h
chlorine	1 kg/h
hydrogen sulphide	1 kg/h
sum of organic substances of class 1 (see Table 62) calculated as total organic carbon	1 kg/h
sum of organic substances of class 1, 2 and 3 (see Table 62) calculated as total organic carbon	10 kg/h

For dust the mass flow, which requires a continuous measurement of the dust concentration in the exhaust gas is 5 kg/h. Between a mass flow of 2 and 5 kg/h the dullness of the exhaust gas should be measured continuously.

7.2 Water

The discharge of waste water in running water or the public sewage system in Austria is regulated with the ordinance “Allgemeine Abwasseremissionsverordnung” (BGBl. 1996/186) and special ordinances for different industrial sectors. These ordinances are based on the Austrian “Wasserrechtsgesetz” BGBl. 1959/215 i.d.F. BGBl. I 2000/90 (water right act). Special ordinances that are of interest for plants producing organic chemicals are:

- Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von Kohlenwasserstoffen und organischen Grundchemikalien BGBl. II 1999/7 (Ordinance for the limitation of waste water emissions from the production of hydrocarbons and basic organic chemicals);
- Verordnung über die Begrenzung von Abwasseremissionen aus der Erdölverarbeitung BGBl. II 1997/344 (Ordinance for the limitation of waste water emissions from oil refining);
- Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von technischen Gasen BGBl. 1996/670 (Ordinance for the limitation of waste water emissions from the production of industrial gases);
- Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von anorganischen Düngemitteln sowie von Phosphorsäure und deren Salzen BGBl. 1996/669 (Ordinance for the limitation of waste water emissions from the production of inorganic fertilizer or phosphoric acid and its salts).

The following Chapters deal with these ordinances in detail and compare the situation in Austria and Germany for the production of hydrocarbons and basic organic chemicals.

7.2.1 Hydrocarbons and basic organic chemicals

The ordinance “Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von Kohlenwasserstoffen und organischen Grundchemikalien” (BGBl. II 1999/7) regulates the emission standards for the production of hydrocarbons and basic organic chemicals. This ordinance came into force at the 13.1.2000. Plants, which have been approved before this date have to fulfil these requirements within the next six years. This ordinance regulates:

- 1) Storage of products from the processing of crude oil or crude oil fractions, which are used in the production processes of item 2 to 6;
- 2) Production of alkenes, alkynes or aromatics from processing products of crude oil or crude oil fractions with cracking, using additional steam (steam cracking);
- 3) Production of chemically pure hydrocarbons or their mixtures from cracking products of item 2 by using physical separation processes;
- 4) Production of basic organic chemicals from products of item 2 or 3 using alkylation, desalkylation, dehydrogenation, disproportionation, hydration, hydroxylation, hydrodesalkylation, hydrogenation, isomerization, oxidation or etherification;
- 5) Production of nitrogen containing basic organic chemicals from hydrocarbons of item 2 or 3 or from substances of item 4 (e. g. amides, amines, cyanates, isocyanates, lactams, nitriles, nitro-, nitroso or nitrate compounds, nitrogen containing aromatics);
- 6) Production of sulphur or phosphorus containing basic organic chemicals from hydrocarbons of item 2 or 3 or from substances of item 4 ;
- 7) Production of halogenated basic organic chemicals from hydrocarbons of item 2 or 3 or from substances of item 4;

- 8) Storage of products from item 2 to 7;
- 9) Cleaning of drawing-off air and aqueous condensates from actions according to item 1 to 8;
- 10) Cleaning of combustion gases from actions according to item 1 to 8 with the use of aqueous substances if simultaneously physical or chemical reactions with the aim of a synthesis or production are made or if the exhaust gas of the combustion is mixed with an other waste gas and the composition of the residual exhaust gas is significantly different compared to the composition of the combustion gas.

The emission standards of this ordinance are presented in Table 67. Different emission standards are provided for the discharge in running water or for the discharge in the public sewage system.

Table 67: Emission standards for the production of hydrocarbons [BGBl. II 1999/7]

general parameters	standards for the discharge in running waters	standards for the discharge in the public sewage system
temperature	30 °C	40 °C
toxicity to algae G_A	8	no impairment of the public waste water treatment plant
toxicity to bacteria G_L	4	no impairment of the public waste water treatment plant
toxicity to daphnia G_D	4	no impairment of the public waste water treatment plant
toxicity to fish G_F	2	no impairment of the public waste water treatment plant
filter out matter	30 mg/l	150 mg/l
pH – value	6.5 – 8.5	6.5 – 10
inorganic parameters	standards for the discharge in running waters	standards for the discharge in the public sewage system
aluminium (calculated as Al)	2 mg/l	limited with the standard for filterable substances
lead (calculated as Pb)	0.5 mg/l	0.5 mg/l
iron (calculated as Fe)	3.0 mg/l	limited with the standard for filterable substances
copper (calculated as Cu)	0.5 mg/l	0.5 mg/l
nickel (calculated as Ni)	0.5 mg/l	0.5 mg/l
mercury (calculated as Hg)	0.01 mg/l	0.01 mg/l
zinc (calculated as Zn)	1 mg/l	1 mg/l
tin (calculated as Sn)	1 mg/l	1 mg/l
ammonium (calculated as N)	5 mg/l	
chloride (calculated as Cl)	limited with standards for toxicity	–
cyanide (easily released and calculated as CN)	0.1 mg/l	0.5 mg/l
fluoride (calculated as F)	30 mg/l	30 mg/l

inorganic parameters	standards for the discharge in running waters	standards for the discharge in the public sewage system
total bound nitrogen (including ammonium, nitrite and nitrate nitrogen)	40 mg/l	–
total phosphorus (calculated as P)	2 mg/l	–
sulphate (calculated as SO ₄)	–	200 mg/l
sulphide (easily released and calculated as S)	0.5 mg/l	1 mg/l
organic parameters	standards for the discharge in running waters	standards for the discharge in the public sewage system
total organic carbon (calculated as C)	25 mg/l	–
COD (calculated as O ₂)	75 mg/l	–
BOD ₅ (calculated as O ₂)	20 mg/l	–
AOX (calculated as Cl)	0.5 mg/l	0.5 mg/l
sum of hydrocarbons	5 mg/l	20 mg/l
POX (calculated as Cl)	0.1 mg/l	0.1 mg/l
phenolindex (calculated as phenol)	0.2 mg/l	20 mg/l
sum of anionic and not ionic tensides	2 mg/l	no impairment of the public waste water treatment plant
sum of volatile aromatics (BTXE)	0.1 mg/l	1 mg/l

Waste water from the production of the following substances has to observe the following special emission limits. The production specific emission limits are related to the installed production capacity in tonnes.

Table 68: Emission limits for the production of several organic substances [BGBl. II 1999/7]

substance	emission standard	emission standard
1. ethylbenzene, cumene	1.0 mg/l	20 g/t
2. acetaldehyde, vinyl acetate	1.0 mg/l	30 g/t
3. vinyl chloride	1.0 mg/l	2 g/t
4. trichlorophenols (TCP, all isomers)	1.0 mg/l	20 g/t
5. trichlorobenzenes (TCB, all isomers)	0.2 mg/l	2 g/t
6. tetrachloromethane	1.5 mg/l	3 g/t
7. hexachlorobutadiene (HCBd)	1.5 mg/l	2 g/t
8. ethane 1,2 dichloride (EDC)	1.0 mg/l	2 g/t
9. trichlorethylene (TRI)	1.0 mg/l	3 g/t
10. perchloroethylene (PER)	1.0 mg/l	3 g/t
11. halogenated organic solvents except: 1,2,4, trichlorobenzene and items 6 – 11	1.0 mg/l	10 g/t

To meet the emission limits of Table 67 and Table 68 four of five successive measured values have to be lower than the emission limit and only one measured value may exceed the emission limit (in maximum 50 % of the emission limit). Most of the parameters have to be determined with mass proportional homogeneous daily average samples. The parameters temperature, filter out matter, pH – value, cyanide, sulphide, POX and sum of volatile aromatics (BTXE) have to be determined with random samples.

7.2.2 Acetylene

For the production of acetylene with calcium carbide as raw material emission limits are set in the “Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von technischen Gasen” (BGBl. 1996/670). All acetylene plants in Austria use calcium carbide processes for acetylene production (see also Chapter 2.3). Table 69 presents the emission standards for discharge of wastewater into running water or into the public sewage system.

Table 69: Emission standards for the production of acetylene from calcium carbide [BGBl. 1996/670]

general parameters	standards for the discharge in running waters	standards for the discharge in the public sewage system
temperature	35 °C	40 °C
toxicity to bacteria G _L	4	no impairment of the public waste water treatment plant
toxicity to fish G _F	2	no impairment of the public waste water treatment plant
filter out matter	50 mg/l	no impairment of the operation of the public sewage system or wastewater treatment plant
pH – value	6.5 – 9	6.5 – 10
inorganic parameters	standards for the discharge in running waters	standards for the discharge in the public sewage system
iron (calculated as Fe)	2 mg/l	limited with the standard for filterable substances
ammonium (calculated as N)	10 mg/l	–
cyanide (easy to release and calculated as CN)	0.1 mg/l	0.1 mg/l
total phosphorus (calculated as P)	1 mg/l	–
sulphate (calculated as SO ₄)	–	200 mg/l
sulphide (calculated as S)	0.1 mg/l	1 mg/l
sulphite (calculated as SO ₃)	1 mg/l	10 mg/l
organic parameters	standards for the discharge in running waters	standards for the discharge in the public sewage system
COD (calculated as O ₂)	50 mg/l	–
sum of hydrocarbons	10 mg/l	20 mg/l
phenolindex (calculated as phenol)	0.1 mg/l	10 mg/l

To meet the emission limits of Table 69 four of five successive measured values have to be lower than the emission limit and only one measured value may exceed the emission limit (in maximum 50 % of the emission limit). Most of the parameters have to be determined with mass proportional homogeneous daily average samples. The parameters temperature, filter out matter, pH – value, cyanide, and sulphide have to be determined with random samples. Further parameters that are not included in this ordinance are regulated by the “Allgemeine Abwasseremissionsverordnung” (BGBl. 186/1996).

7.2.3 Melamine and Urea

In Austria the ordinance “Verordnung über die Begrenzung von Abwasseremissionen aus der Herstellung von anorganischen Düngemitteln sowie von Phosphorsäure und deren Salzen “ (BGBl. 1996/669) regulates the emission standards for the discharge of waste water from melamine and urea production. Table 70 presents these emission standards.

Table 70: Emission standards for waste water from urea and melamine production [BGBl. 1996/669]

general parameters	standards for the discharge in running water	standards for the discharge in the public sewage system
temperature	30 °C	35 °C
toxicity to fish G_F	4	no impairment of the public waste water treatment plant
filter out matter	30 mg/l	150 mg/l
pH-value	6.5 – 8.5	6.5 – 9.5
inorganic parameters	standards for the discharge in running water	standards for the discharge in the public sewage system
ammonium (calculated as N)	0.5 kg/t	0.5 kg/t
nitrate (calculated as N)	0.5 kg/t	0.5 kg/t
nitrite (calculated as N)	0.02 kg/t	0.02 kg/t
organic parameters	standards for the discharge in running water	standards for the discharge in the public sewage system
COD (calculated as O ₂)	0.5 kg/t	–

The emission standards are related to the installed production capacity of the plant (related to the tonne nitrogen in the final product). To meet the emission limits of Table 70 four of five successive measured values have to be lower than the emission limit and only one measured values may exceed the emission limit (in maximum 50 % of the emission limit). Most of the parameters have to be determined with mass proportional homogeneous daily average samples. The parameters temperature, filter out matter, pH – value and nitrite have to be determined with random samples.

Further parameters that are not included in this ordinance are regulated by the “Allgemeine Abwasseremissionsverordnung” (BGBl. 1996/186).

7.3 Waste

In some production processes of the chemical industry a lot of waste is produced. Hazardous waste as well as non hazardous waste could be produced in large amounts. Especially in the chemical industry solvent residues or distillation residues are co-incinerated or incinerated in several plants.

In the “waste management act” (BGBl. 1990/325 i.d.F. BGBl. I 2000/90) of Austria the principles of the waste management in Austria are regulated. The three major principles are listed below.

1.) Avoidance of waste

- Qualitative waste avoidance, that means the substitution of environmental hazardous substances with environmental acceptable substances. Small amounts of certain substances (e. g. toxic heavy metals or halogenated organic compounds) cause superproportional high nuisances and superproportional high costs for waste disposal;
- Quantitative waste avoidance, that means partial or total renunciation of substances or processes that produce wastes.

2.) Treatment of waste

- Utilization of secondary raw materials (e. g. recycling of metals, glass or paper)
- Utilization of biogenous wastes (e. g. compost preparation from biogenous wastes)
- Utilization of energy (e. g. combustion with waste heat recovery)

3.) Disposal of waste

- Inerting (e. g. thermal treatment with subsequent dumping of the treated ash)
- Immobilisation (e. g. fixing of inorganic pollutants into a silicate structure)
- Dumping (limitation on controlled dumping of earth crust like residues)

For incineration or co-incineration of hazardous wastes two ordinances (BGBl. II 1999/22 and BGBl. II 1999/32) regulate the emission limits in Austria since 1999. These ordinances have been enacted to transpose the council directive 94/67/EG of 16 December 1994 concerning the combustion of hazardous waste. All emission limits are related to dry exhaust gas and an oxygen content of 11 %. Table 71 presents the emission limits for such plants.

Table 71: *Emission limits for the co-incineration of hazardous wastes in combustion plants [BGBl. II 1999/22]*

component	half hourly mean value	day mean value
dustlike emissions	10 mg/m ³	10 mg/m ³
gaseous and vaporous organic substances (calculated as total fixed organic carbon)	10 mg/m ³	10 mg/m ³
hydrogen chloride	10 mg/m ³	10 mg/m ³
hydrogen fluoride	0.7 mg/m ³	0.5 mg/m ³
sulphur dioxide (calculated as SO ₂)	50 mg/m ³	50 mg/m ³

component	half hourly mean value	day mean value
nitrogen oxides (NO and NO ₂) (calculated as NO ₂)	400 mg/m ³	200 mg/m ³
V _{waste gas} ≥ 5 000 m ³ /h	300 mg/m ³	200 mg/m ³
V _{waste gas} ≥ 10 000 m ³ /h		
new plants	100 mg/m ³	70 mg/m ³
existing plants	150 mg/m ³	150 mg/m ³
carbon monoxide	100 mg/m ³	50 mg/m ³
ammonia ⁴²	10 mg/m ³	5 mg/m ³
	mean value of a period between 0.5 and 8 hours	
cadmium and thallium and their compounds (calculated as Cd and Tl)	0.05 mg/m ³	
mercury and its compounds (calculated as Hg)	0.05 mg/m ³	
the sum of antimony, arsenic, lead, chromium, cobalt, copper, manganese, nickel, vanadium, tin and their compounds (calculated as Σ Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn)	0.5 mg/m ³	
	mean value of a period between 6 and 8 hours	
PCDD/F's (calculated as 2,3,7,8 TCDD toxic equivalent)	0.1 ng/m ³	

⁴² If ammonia or similar substances are used for DeNO_x measures

8 LIST OF ABBREVIATIONS

ANU	...	A mt für N atur- und U mweltschutz
AOX	...	A dsorbable o rganic halogens (X)
BAT	...	B est A vailable T echniques
BOD	...	B iological O xygen D emand
BRef	...	B AT R eference
BTX	...	B enzene T oluene X ylene
COD	...	C hemical O xygen D emand
EDC	...	E thylene 1,2 d ichloride
EIPPCB	...	E uropean I PPC B ureau
GMHA	...	G lyoxylic acid m ethyl ester methyl h emiacetal
HCBD	...	H exachlorobutadiene
IEF	...	I nformation E xchange F orum
IFP	...	I nstitute F rancais du P etrole
IPPC	...	I ntegrated P ollution P revention and C ontrol
IPTS	...	I nstitute for P rospective T echnological S tudies
LPG	...	L iquefied P etroleum G as
LVOC	...	L arge V olume O rganic C hemicals
MTBE	...	M ethyl tertiary B utyl E ther
NMP	...	N – M ethylpyrrolidone
PER	...	P erchloroethylene
POX	...	P urgeable o rganic halogens (X)
PSA	...	P hthalsäureanhydrid
TCB	...	T richlorobenzene
TCP	...	T richlorophenol
TRI	...	T richlorethylene
VAM	...	V inyl a cetate m onomer
VOC	...	V olatile O rganic C arbon
WW & WGT	...	W aste W ater & W aste G as T reatment

9 LITERATURE

Introduction:

UBA GERMANY, (1999): Information of the Federal Environment Agency of Germany submitted to the Technical Working Group on Large Volume Organic Chemicals.

ÖSTAT, (1999): Konjunkturstatistik im produzierenden Bereich 1997 und 1998 (Sachgüter sowie Bauwesen. Band 2 Ergebnisse auf Betriebsebene, Verlag Österreich, Wien.

WKÖ, (2000): Homepage der Wirtschaftskammer Österreichs Fachverband der chemischen Industrie. www.wk.or.at/fcio.

Ethylen and Propylene:

WWW.CEFIC.BE, (1999): Homepage of Cefic, APPE Annual Report 1997-1998.

WINNACKER, K., HARNISCH, H. & STEINER, R. (1981a): Chemische Technologie. Band 5, p. 184, 4. Auflage. Carl Hanser Verlag, München.

WITZLEB, V. & HEISEL, M. (1997): Ablaugeoxidationsanlage mit Restgasverbrennung für die Sächsische Olefinwerke GmbH in Böhlen. Berichte aus Wissenschaft und Technik. Heft 75/97, p. 13-16 Linde AG.

WINNACKER, K.; HARNISCH, H. & STEINER, R. (1981b): Chemische Technologie. Band 5, p. 232, 4. Auflage. Carl Hanser Verlag, München.

FB9-TC2.CHEMIE.UNI-OLDENBURG.DE, (1999): Homepage der "Carl von Ossietzky Universität Oldenburg".

KRAUSE, G. & PETZNY, W. J. (1993): Petrochemie und integrierter Umweltschutz. Erdöl, Erdgas, Kohle, 109. Jahrgang, Heft 2, p. 90-94, Urban Verlag, Wien Hamburg.

FRANKE, M.; BERNA, J. L.; CAVALLI, L.; RENTA, C.; STALMANS, M. & THOMAS, T. (1995): A Life-Cycle Inventory for the Production of Petrochemical Intermediates in Europe. Tenside Surfactants Detergents, Bd. 32: 384-396, Carl Hanser Verlag, München.

BAIRLEIN, W.; WEIDENHAMMER, H. F. & WIMMER J. P. (1997): Fackellooses Anfahren von Ethylenanlagen. Berichte aus Technik und Wissenschaft, Bd. 76, p. 41-45, LINDE AG.

BAUR, K. (1997): Entstehung und Verhalten von sauerstoffhaltigen organischen Verbindungen in Ethylenanlagen. Berichte aus Technik und Wissenschaft, Bd. 76, p. 25-27, LINDE AG.

UBA (2000): Stand der Technik bei Raffinerien im Hinblick auf die IPPC – Richtlinie. Monographie 119, Federal Environment Agency of Austria, Vienna.

C₄ Fraction:

WEISSERMEL, K. & ARPE, H. J. (1998a): Industrielle organische Chemie. p. 119, VCH, Weinheim.

WINNACKER, K.; HARNISCH, H. & STEINER, R. (1981): Chemische Technologie. Band 5, p. 237, 4. Auflage. Carl Hanser Verlag, München.

WWW.CEFIC.BE, (1999): Homepage of Cefic, APPE Annual Report 1997-1998.

WEISSERMEL, K. & ARPE, H. J. (1998b): Industrielle organische Chemie. p. 76, VCH, Weinheim.

FB9-TC2.CHEMIE.UNI-OLDENBURG.DE, (1999): Homepage der "Carl von Ossietzky Universität Oldenburg".

Acetylene:

WINNACKER, K.; HARNISCH, H. & STEINER, R. (1981): Chemische Technologie. Band 5: p. 194-195, 4. Auflage. Carl Hanser Verlag, München.

BTX:

- WEISSERMEL, K. & ARPE, H. J. (1998a): Industrielle organische Chemie. p. 345, VCH, Weinheim.
- WWW.CEFIC.BE, (1999): Homepage of Cefic, APPE Annual Report 1997-1998.
- WEISSERMEL, K. & ARPE, H. J. (1998b): Industrielle organische Chemie. p. 348, VCH, Weinheim.
- WEISSERMEL, K. & ARPE, H. J. (1998c): Industrielle organische Chemie. p. 351, VCH, Weinheim.
- WINNACKER, K.; HARNISCH, H. & STEINER, R. (1981a): Chemische Technologie. Band 5, p. 249, 4. Auflage. Carl Hanser Verlag, München.
- WEISSERMEL, K. & ARPE, H. J. (1998d): Industrielle organische Chemie. p. 353, VCH, Weinheim.
- WINNACKER, K.; HARNISCH, H. & STEINER, R. (1981b): Chemische Technologie. Band 5, p. 256, 4. Auflage. Carl Hanser Verlag, München.
- FRANKE, M.; BERNA, J. L.; CAVALLI, L.; RENTA, C.; STALMANS, M. & THOMAS, T. (1995): A Life-Cycle Inventory for the Production of Petrochemical Intermediates in Europe. Tenside Surfactants Detergents, Bd. 32: 384-396, Carl Hanser Verlag, München.
- WWW.CEFIC.BE, (1999): Homepage of Cefic, APPE Annual Report 1997-1998.
- WINNACKER, K.; HARNISCH, H. & STEINER, R. (1981c): Chemische Technologie. Band 5, p. 252, 4. Auflage. Carl Hanser Verlag, München.

Formaldehyde:

- WEISSERMEL, K. & ARPE, H. J. (1998): Industrielle organische Chemie. VCH, Weinheim.
- KREMS Chemie (1999): Informations to the questionnaire of the Federal Environment Agency of Austria.
- PUXBAUM, H. & ELLINGER, R. (1997a): Gutachten über Emissionsmessungen an den vier Schwachgasmotoren zur Eigenstromerzeugung der Krems Chemie AG im Standort 3500 Krems – Hafenstrasse 77.
- KREMS Chemie (1998): Firmenprospekt Innovative Energiegewinnung "Das Schwachgas-Kraftwerk der Krems Chemie".
- PUXBAUM, H. & ELLINGER, R. (1998): Messbericht über Emissionsmessungen am Kessel K3 der Krems Chemie AG im Standort 3500 Krems – Hafenstrasse 77, gemäß den bescheidmäßigen Anforderungen.
- PUXBAUM, H. & ELLINGER, R. (1997b): Messbericht über Emissionsmessungen am Kessel K2 der Krems Chemie AG im Standort 3500 Krems – Hafenstrasse 77, gemäß den bescheidmäßigen Anforderungen.

MTBE:

- ROSSINI, S.; MARCHIONNA, M.; PESCAROLLO, E.; PICCOLI, V.; SANFILIPPO, D. & TROTTA, R. (1998): Ether Synthesis From C₄ Streams: A Highly Integrated and Versatile Technology Portfolio. Erdöl, Erdgas, Kohle, Bd. 114 Heft 7/8: 381-384, Urban Verlag, Wien Hamburg.
- BREJC, S.; HOFMANN, H.; GOTTLIEB, K. & SIMO, T. (1994): Untersuchungen zu einem alternativen Syntheseweg für MTBE. Erdöl und Kohle – Erdgas, Bd. 47 Heft 2: 51-55, VCH, Weinheim Hamburg.
- WEISSERMEL, K. & ARPE, H. J. (1998): Industrielle organische Chemie. p. 79, VCH, Weinheim.

Maleic Anhydride:

- ULLMANN'S, (1978): Ullmann's Encyklopädie der technischen Chemie. Bd. 16: 409. 4. Auflage, VCH, Weinheim.

BUA (1988): Benzol – Stoffbericht 24. Beratergremium für umweltrelevante Altstoffe (BUA) der Gesellschaft deutscher Chemiker (ed.), VCH, Weinheim.

WEISSERMEL, K. & ARPE, H. J. (1998): Industrielle organische Chemie. p. 408, VCH, Weinheim.

DSM Chemie Linz GmbH, (1998): Emissionskataster der DSM Fine Chemicals Austria 1998.

DSM Fine Chemicals Austria, (2000): Vereinfachte Umwelterklärung 2000.

ANU, (1999): Amtsgutachten des Amtes für Natur- und Umweltschutz des Magistrat Linz.

Phthalic Anhydride:

WWW.CEFIC.BE, (1998): Homepage of Cefic, APPE Annual Report 1997-1998.

WWW.PROCESS-ECONOMICS.COM, (1998): Homepage of SRI Consulting, Abstract of the Process Economics Program Report 34B Phthalic Anhydride.

LENZ, H.; MOLZAHN, M. & SCHMITT, D. W. (1989): Produktionsintegrierter Umweltschutz – Verwertung von Reststoffen. Chemie-Ingenieur-Technik, Bd. 61: 860-866. VCH, Weinheim.]

ATMOSA Petrochemie, (1999): Informations to the questionnaire of the Federal Environment Agency of Austria.

Niederösterreichische Umweltschutzanstalt, (1996): Messbericht über die Emissionsmessungen an der Phthalsäure-Anhydrid-Anlage der Fa. Atmosa Ges.m.b.H. in Schwechat Mannswörth.

Glyoxylic Acid:

DSM Chemie Linz GmbH, (1999): Emissionskataster der DSM Fine Chemicals Austria 1998.

DSM Fine Chemicals Austria, (2000): Vereinfachte Umwelterklärung 2000.

Urea:

AGROLINZ Melamin, (1999): Informations to the questionnaire of the Federal Environment Agency of Austria.

EFMA, (1995): Production of Urea and Urea Ammonium Nitrate.

Melamine:

AGROLINZ Melamin, (1999): Informations to the questionnaire of the Federal Environment Agency of Austria.

AGROLINZ Melamin, (1997): Emissionserklärung of the AGROLINZ Melamin GmbH.

Generic BAT:

1. Draft WW & WGT, (2000a): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. European IPPC Bureau, Seville, Spain.

1. Draft REFINERIES, (2000): 1. Draft of BRef on Refineries. European IPPC Bureau, Seville, Spain.

1. Draft LVOC, (2000a): 1. Draft of BRef on BAT in the Large Volume Organic Chemical Industry. European IPPC Bureau, July 2000, Seville, Spain.

CONCAWE, (2000): in 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector, page 150, European IPPC Bureau, May 2000.

INFOMIL, (1999): Dutch Notes on BAT for Mineral Oil Refineries. p. E–5, The Hague, Netherlands.

- UK EA, (1999): in 1. Draft of the BRef on BAT in the Large Volume Organic Chemical Industry. p. 95, European IPPC Bureau, July 2000, Seville, Spain.
- UBA, (2000a): Stand der Technik bei Raffinerien im Hinblick auf die IPPC Richtlinie. Monographie 119, p. 139, Umweltbundesamt Wien.
1. Draft WW & WGT, (2000b): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 189, European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000c): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 195, European IPPC Bureau, Seville, Spain.
- UBA, (2000b): Stand der Technik bei Raffinerien im Hinblick auf die IPPC Richtlinie. Monographie 119, p. 142, Umweltbundesamt Wien.
1. Draft WW & WGT, (2000d): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 207, European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000e): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 209, European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000f): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 211, European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000g): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 213, European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000h): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 215, European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000i): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 161, European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000j): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 172, European IPPC Bureau, Seville, Spain.
- BRef Cement & Lime, (2000): BAT Reference Document on the production of Cement and Lime. European IPPC Bureau, Seville, Spain.
- BRef Glass, (2000): BAT Reference Document on the production of Glass. European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000k): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 168, European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000l): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 219, European IPPC Bureau, Seville, Spain.
1. Draft WW & WGT, (2000m): 1. Draft of BRef on Common waste water and waste gas treatment/management systems in the chemical sector. p. 223, European IPPC Bureau, Seville, Spain.
1. Draft LVOC, (2000b): 1. Draft of BRef on BAT in the Large Volume Organic Chemical Industry. p. 95, European IPPC Bureau, July 2000, Seville, Spain.
- UBA, (2000c): In Österreich eingesetzte Verfahren zur Dioxinminderung. Monographie 116, Umweltbundesamt Wien.

Legislation:

TA – LUFT, (1986): Technische Anleitung zur Reinhaltung der Luft – TA – Luft vom 27.02.1986 (Technical Instructions on Air Quality Control).