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Process Agents Task Force

Case Study #8

Production of Poly-Phenylene-Terephtal-Amide with the aid of CTC in an intermediate raw product

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CS-8 Production of Poly-Phenylene-Terephtal-Amide with the aid of CTC in an intermediate raw product

CS-8.1 Introduction

The aromatic polymer PPTA (**P**oly-**P**henylene-**T**erephtal-**A**mide) is produced in the Netherlands from an intermediate raw material that is produced using carbon tetrachloride (CTC) as a process agent.

CS-8.1.1 Products

PPTA fibres have are used in a wide variety of high tech applications requiring extreme strength (5 times as strong as steel at the same weight), high tensile modulus, good chemical stability, very low creep rate, good dielectric properties, high flame resistance and self extinguishing and others unique properties.

CS-8.1.2 Application

PPTA can be successfully used in complex products with rubber and synthetic materials and in composed textures, or combined with existing materials to improve properties.

In combination with steel, the fibre is used for impact shields to give protection for equipment and vehicles. This means that military, police and civilian vehicles can be armoured and yet be 30-60% lighter and more manoeuvrable than with traditional armour. The material also provides lightweight body protection for motorcycling and for police and military (a 100% better ballistic performance than a steel helmet as well as flexible, bullet and fragment resistant vests which are easy to wear). It is also used in aircraft, railway, and road vehicles to shield against piercing from equipment failure such as aircraft engine disintegration (turbine blade failure)

Reinforced refrigerator trailers are some 25% less in weight, are better-insulated and less sensitive to damage. Savings result from a lighter weight, smaller refrigerator with greater payload.

Optical fibre cables can be made lighter in weight and rodent resistant.

Better performance is achieved for rubber transmission belts, hydraulic hoses, automotive hoses, conveyor belts and ultra lightweight automobile tires. Lightweight automobile tires have lower fuel consumption.

Wood laminates can replace hardwood applications without loss of strength (for instance large warehouses).

The PPTA fibre replaces asbestos for brake linings, brake blocs and disk brake pads; for chemical resistant gaskets; and for heat resistant workwear and fire blankets.

There is a growing market for these applications.

CS-8.2 The manufacturing process

The polymer is produced from the raw materials PPD (para-phenylenediamine) and TDC (terephtaloyldichloride). The raw materials PPD and TDC are produced at the same facility.

The only use of CTC is in the production of TDC. TDC is produced by side chain chlorination of p-Xylene in CTC followed by fusion with terephtalic acid. Purification is by distillation; hydrochloric acid (muriatic acid) is produced as a by-product. CTC is separated from product streams and recycled constantly in the process. It is regenerated for reuse by distillation. The CTC distiller waste is incinerated. All waste streams (gas and liquid) are purified. Wastewater and vent gases are purified in an integrated system by air stripping and active carbon adsorption. Active carbon is regenerated with steam; the condensed CTC is recycled. The Hydrochloric acid (HCl) is purified by steam stripping and the recovered CTC is recycled, see flow chart. The entire process is contained.

CS-8.3 Why CTC is used

CTC is used for the following reasons:

1. To avoid side reactions during chlorination which is crucial for the polymerisation.

2. To reduce explosion and fire risks during chlorination.

3. To reduce waste and increase yield by acting as a carrier for recycling of incomplete chlorination products.

4. To clean HCl emerging from the reactors (the cleaning solution is recycled).

CTC process agents are the only option that satisfies these safety, waste-reduction, and quality purposes under the various conditions of the process:

1 CTC is inert in all process steps;

2 CTC prevents side reactions in the reactor;

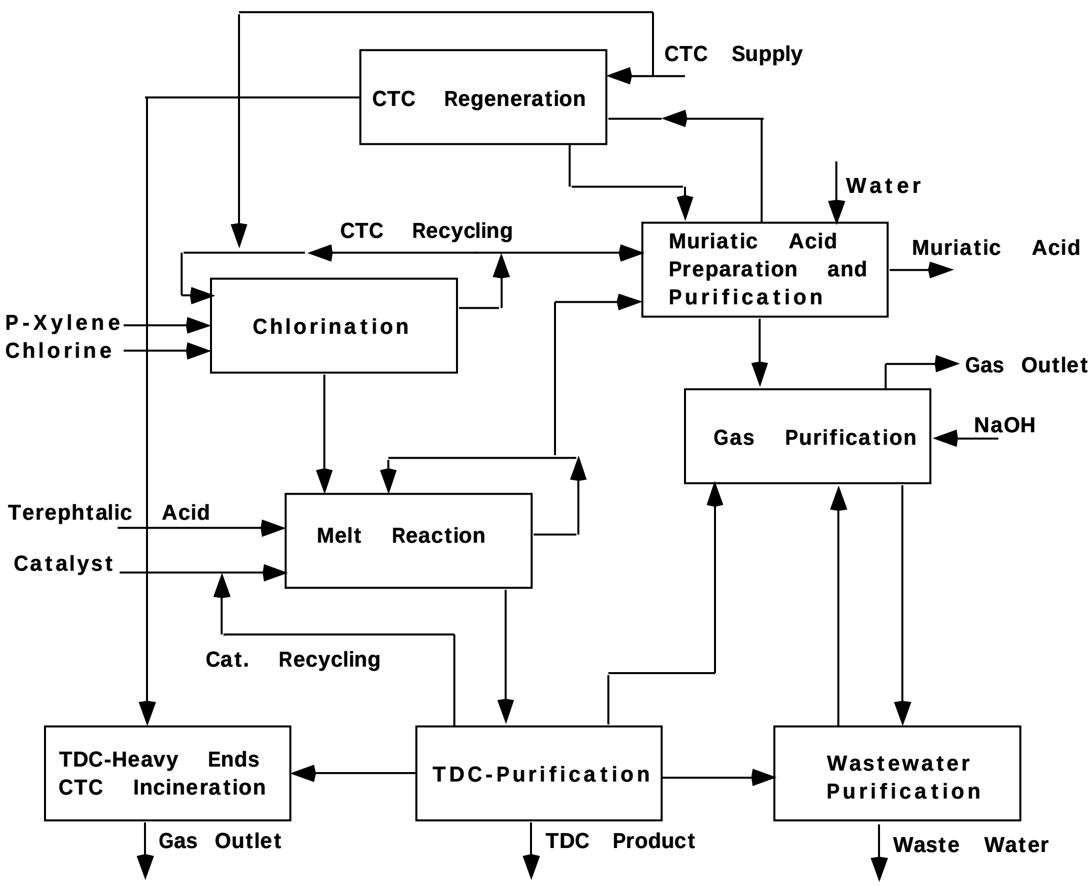
3 CTC has the right vapour pressure to prevent explosions in the gas cap of the reactor;

4 CTC is easy to recover and reuse; and

5 CTC has a low solubility in HCl.

As a consequence the use of CTC from the start of the TDC-plant has been fully integrated in the process.

TDC Process for Aramid polymer Production



CS-8.4 How CTC is used

The "make-up" quantity (1995) is 72.5 tons per year, mainly arising from the destruction of CTC distillers waste (the unusable bottom fraction that remains in distilling the recycled CTC). Since 1995 processoptimalisations lead to less make-up per year, under normal conditions. In 2000 the make-up was approximately 10 ton.

Source	Name	CTC Emissions	Remarks

		ton/year	
Product	TDC	0	
Product	30% HCl	0.240	Maximum
Wastewater	after treatment	0.060	Maximum
Vent gas	after treatment	2	Further emission reduction foreseen
Diffuse	losses in collecting system	Parts/million	Project underway to for total containment
Leakage	losses	0.030	Estimates based on. EPA calculations
Incidental	losses	0.200	Emissions result from entry required for maintenance
Waste	incineration	70	
Required	Make-up	72.5	(Base year 1995)

CS-8.5 Pollution abatement

- Since 1990 when the Montreal Protocol was amended to add carbon tetrachloride (CTC) to the list of controlled substances, efforts have been underway to reduce emissions in the existing TDC-plant, and to eliminate CTC.

CS-8.5.1 The emission reduction effort has led to the following results:

- The CTC discharge in wastewater was reduced by 99% by redesign and installing more separators for CTC.
- The CTC discharge in waste gas was reduced by over 99% by investigation and redesign.
- Liquid and gas flow systems were simplified to facilitate recycling.
- All waste streams are monitored.
- Wastes containing CTC are incinerated by a UNEP-accepted technique.
- The CTC content of HCl was reduced with the aid of monitoring.

- Diffuse losses were measured and reduced to some 60 kg/year (calculated according to correlated emission factors).

- The environmental management system has been certified under ISO 14001.

Emissions for 1990, 1995 en 2000 in tons of CTC/year:

Source	Name	1990	1995	2000
Product	30% HCl	0.45	0.12	0.12
Wastewater	After treatment	1.680	0.06	<0.01
Vent gas	After treatment	35	1.62	0.36
Diffuse	Losses	0.54	0.03	0.06
Incidental	Losses	0.20	0.20	0.02
Total emission		37.87	2.03	0.44

CS-8.5.3 Regulatory Compliance

Corporate investment in response to national environmental regulations together with the decisions of the Montreal Protocol has directly and indirectly reduced emissions as documented on the following table.

#	Type of law[1)]	Conditions	Applied technique	Results[2)]
1	Restriction of water pollution	Reduce existing pollution 50 - 90%	Separators followed by air stripper	99% reduction
2	Restriction on air pollution	Reduce existing Pollution to standard to max. 20 mg/m3	Active carbon adsorbers, contain-ment	1995: 99% reduction; ongoing program
3	Unpolluted products	max. 10 mg/kg	steam stripper	Well below 10 mg/kg
4	Waste destruction to standard	According to Dec IV/11	Incinerator	Destruction more than 99,9%
5	Unpolluted soil	No polluted soil	impenetrable slabs with water collecting provisions	No pollution

1 There is a voluntary convention between government and the chemical industry to reduce emissions to as low as is feasible, according best available techniques.

2 Monitoring has added a lot to good and reliable results.

CS-8.6 Future efforts to reduce emissions

In the near future emissions will be further reduced:

- The vent gas purification will be improved on the basis of placing an extra purification unit
- Research activities continue to eliminate CTC in the TDC process
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- CTC quantities will be reduced in the purification unit
- Leakage by diffusion will be further reduced as plant is upgraded
- Processing will be improved to prevent incidental emissions

These improvements are required under terms of the environmental permits (Dutch Air pollution act and water pollution act) and monitoring of the waste streams will be reported to the Dutch government on a quarterly basis for wastewater and for waste gases on a yearly basis.

CS-8.7 ODS-Free Technical Options

There is one commercially proven process to produce PPTA using an alternative process to manufacture the essential raw materials (TDC) without CTC. However, the cost of licensing this technology for competing companies and finding affordable chemicals is not currently uneconomic. Furthermore, the alternative process is based on a different chemical reaction with highly toxic phosgene as a raw material. Moreover, the cost of adopting this process is estimated 150 million US dollars to eliminate just 0.44 metric tonne emission per year. Research continues to find a better ODS-free alternative is not promising.