

# ANALYSIS OF ALTERNATIVES

## (Public Version)

**Legal name of applicant(s):** *DOMO Caproleuna GmbH*

**Submitted by:** *DOMO Caproleuna GmbH*

**Substance:** *Trichloroethylene*

**Use title:** *Industrial use as an extraction solvent for the purification of caprolactam from caprolactam oil*

**Use number:** *9a*

**DECLARATION**

We, DOMO Caproleuna GmbH, request that the information blanked out in the “public version” of the Analysis of Alternatives is not disclosed. We hereby declare that, to the best of our knowledge as of today (August 18<sup>th</sup> 2014) the information is not publicly available, and in accordance with the due measures of protection that we have implemented, a member of the public should not be able to obtain access to this information without our consent or that of the third party whose commercial interests are at stake.

Signature:

August 18<sup>th</sup> 2014



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In this Analysis of Alternative (AoA) the technical and process functions of trichloroethylene (TCE) as an extraction solvent in the purification of caprolactam from caprolactam oil is categorized into three key areas: solute specificity and loading; operational practicality; solvent recovery and recycling. These technical functions have been optimized over the last 20 years by DOMO Caproleuna GmbH to develop a high-integrity, intensive and cost-effective purification process for caprolactam which minimizes both solvent emissions and energy consumption through the recycling process.

From the commencement of caprolactam manufacture at Leuna manufacturing plant, there has been always commercial and technical pressure to identify alternative, less hazardous and more cost-efficient process improvements, including an alternative extraction solvent. As a systematic approach DOMO identified technical criteria to assess the applicability of alternative substance, particularly loading capacity for caprolactam, solvent density and boiling point range (see Table 1.1). In addition, the toxicity profile and flammability of alternative solvents was examined, the latter being important as the current extraction unit at Leuna is not appropriate for the use of flammable solvents.

DOMO has undertaken an extensive literature analysis as well as market analysis to identify all potential alternative extraction solvents and processes. This analysis continues to be updated on a regular annual basis and has been verified by an external consultant in the course of the preparation of this AoA.

The solvent extraction units at DOMO Caproleuna GmbH have been designed and optimised for the use of trichloroethylene as the extractive solvent. The physico-chemical reactions that occur during the extraction process are very complex and the use of a specific solvent, as in this case trichloroethylene, is optimized to produce a pure end-product at high efficiency. Further to this, the specific engineering characteristics of the equipment design prevent simple direct solvent replacement (drop-in solution). As all equipment is optimised for the preferred solvent used, for example the height and diameters of extraction columns based on specific solvent properties, whilst at the same time minimizing losses to the workplace and the environment through good equipment design (BAT) and operational risk management measures.

In comparison with the other solvents used for commercial caprolactam recovery, toluene and benzene, TCE demonstrates superior technical and process functionalities with increased caprolactam loading capacity and

selectivity to produce a final product of higher quality. The higher loading capacity, in combination with the inherent physico-chemical properties of TCE, produces a lower volume solvent recovery and recycle system which minimizes the process energy requirements.

A switch to the current alternative commercial solvents (toluene and benzene) is not suitable on either technical or economic grounds. Additionally, DOMO does not have any access to other commercially used extraction technologies that are used by competitors.

Although toluene is not a carcinogen, it is nonetheless flammable and hazardous to health and offers only a low reduction in overall risk. Toluene has a lower caprolactam loading capacity, resulting in a significant increase in solvent inventory and equipment size as well as increased energy consumption for solvent recycling in order to achieve similar process intensity and productivity as that currently achieved with TCE. This would impose a significant economic burden without leading to any risk reduction.

Benzene is also a carcinogenic substance and there is no benefit in further consideration of this alternative as there is no reduced inherent hazard. Furthermore, benzene is also flammable and does not satisfy the technical and process function criteria as well as TCE.

In addition to the alternative commercial solvents, a significant number of other solvents have been evaluated for their suitability in the extraction of caprolactam from caprolactam oil. The properties of these solvents have been compared with the technical criteria for a replacement extraction solvent and no suitable solvents have been identified to date (see Table 4.18). Mixed solvent systems, in particular alkane/alkanol mixtures, have been evaluated too and show some potential for caprolactam recovery, with a lower solvent toxicity profile and comparable technical functionality. However, the practicalities of engineering a system based on such a mixed solvent have still to be fully evaluated. Major capital and operational costs will be incurred, due to probable increased energy requirements for mixed solvent recovery, which would make a switch to mixed solvent systems economically non- feasible. Such solvent systems are therefore not considered suitable on technical and economic grounds.

**Technically**, trichloroethylene is therefore considered the optimal solvent for caprolactam purification from caprolactam oil due to the high loading capacity and selectivity for caprolactam to achieve a high process intensity, in addition to the physico-chemical properties that determine its effective performance characteristics in counter current extraction and subsequent

solvent recovery processes. This leads to a very economic extraction process, when compared with potential alternative solvents such as toluene and benzene, as the high caprolactam loading capacity leads to a low overall solvent inventory which, in turn, significantly reduces the cost of solvent recovery and recycling.

**Economically**, any substance or process substitution is not feasible due to the high capital replacement and operating costs which cannot be passed on to customers or otherwise absorbed by DOMO.

Additionally it should be noted that under existing legislation referring to the use of chemicals (Chemical Agents Directive 98/24/EC –article 6 and Carcinogens Directive 2004/37/EC – article 4.1) and as transposed into German legislation by the Gefahrstoff-Verordnung (§ 6), each hazardous substance needs to undergo an evaluation for potential substitutes. DOMO documents this for trichloroethylene in a substitution evaluation according to the timing stipulated by the legislation every second year. Hence, had there been a suitable alternative solvent identified DOMO would have been obliged to switch to it already.

A complete description of the technical production process operated by DOMO Caproleuna GmbH can be found in the confidential Annex of the Chemical Safety Report (CSR).

Table 1.1 Summary of Comparison of Potential Alternative Commercial Solvents for the Extraction of Caprolactam from Caprolactam Oil

Solvent Name	CAS No	EC No	BP	Density	Vapour Pressure	Water Solubility	Viscosity	Extraction Efficiency	Caprolactam Loading	Final Purity	Flammability	Comment
			°C	g/ml	hPa @ 20°C	g/l	mPas	%	%			
Trichloroethylene	79-01-6	201-167-4	87	1.465	99	1.1	0.58	97	25	2.3	Non-flammable	Optimum combination of properties
Toluene	108-88-3	203-625-9	110	0.865	29.1	0.5	0.6	79	8	2.8	Flammable	Flammable. Low loading capacity and low density would require complete re-engineering of extraction plant. Higher solvent requirement and higher boiling point would increase cost of solvent recovery
Benzene	71-43-2	200-753-7	80	0.88	100	1.8	0.66	n/a	19	n/a	Flammable	Flammable. Carcinogenic. Low density would require re-engineering of extraction plant
Mixed solvent (heptane:heptanol)	142-82-5 /111-70-6	205-563-8 /203-897-9	113	0.74	80	0.65	1.15	100	3.7	3.7	Flammable	Laboratory evaluation only. Flammable. Low loading capacity and low density would require complete re-engineering of extraction plant. Recovery of mixed solvent would be complex.
<i>Condition for selection of potential alternative</i>			>70<100	>1.3	<100	<1.1		>75	>12.5	<5	<i>Non-flammable</i>	
See below for explanation			A	B	C	D		E	F	G	H	

n/a = not available

- A Highlighted cells indicate solvent BP may be too high for efficient solvent recovery
- B Highlighted cells indicate that solvent density will require re-engineering of counter-current extraction columns
- C Highlighted cells indicate solvent vapour pressure may lead to increased solvent loss
- D Highlighted cells indicate that solvent water solubility is too high for application



**E** Highlighted cells indicate total extraction efficiency, based on DOMO laboratory methodology, may lead to longer contact times for the extraction process

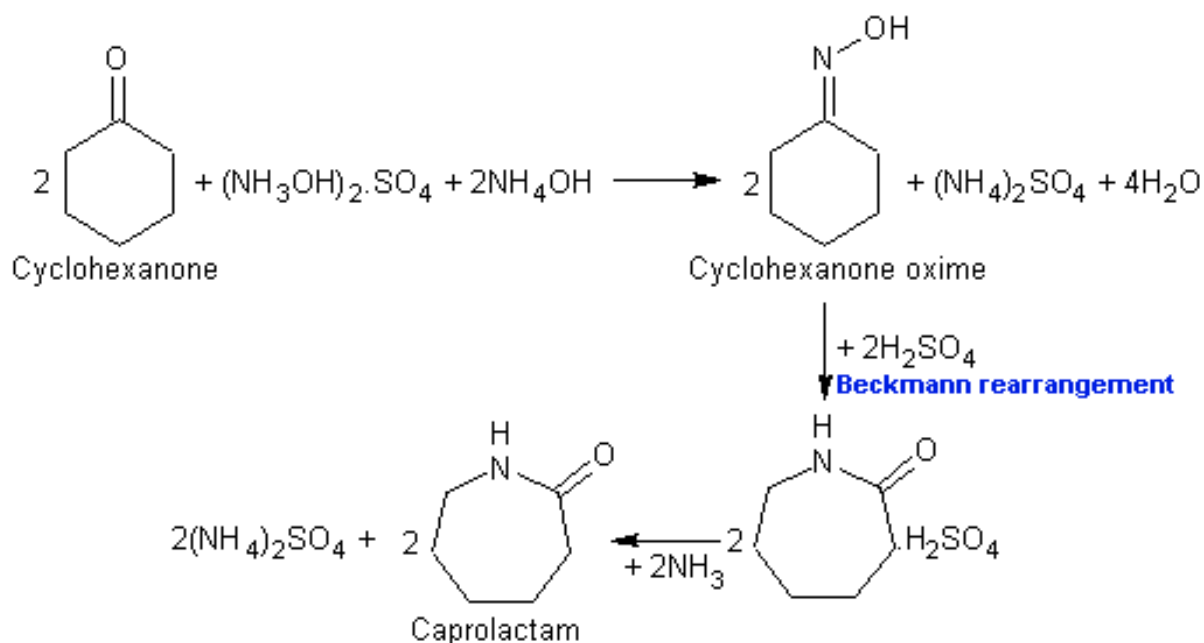
**F** Highlighted cells indicate a loading capacity, determined from test extraction of 50% (w/w) caprolactam in water, that will require at least double the solvent inventory for the same production intensity

**G** Highlighted cells indicate extractive solvents that did not produce a final quality specification of caprolactam based on organic impurities as measured by permanganate number

**H** Highlighted cells indicate solvents that are flammable

At DOMO Caproleuna GmbH, caprolactam is synthesised in two steps from cyclohexanone. In the first step reaction with hydroxylammonium sulphate in the presence of ammonium hydroxide forms the intermediate cyclohexanone oxime, with ammonium sulphate as a by-product. In the second step oleum is added and the oxime undergoes Beckmann rearrangement to produce the sulphate salt of caprolactam. This is neutralised by the addition of aqueous ammonia solution. The reaction scheme is shown in Figure 2.1.

Figure 2.1 *Caprolactam Synthesis*



The reaction process creates a two phase aqueous equilibrium product mixture, with a top phase being rich in caprolactam (65-70% w/w, caprolactam oil) and an ammonium sulphate-rich lower phase containing residual caprolactam (approximately 1%) and ammonium sulphate (40% w/w).

To recover the caprolactam, the top phase, also known as caprolactam oil, is extracted with an organic solvent in a counter-current extraction process. A subsequent washing stage with water removes some of the impurities from the organic solvent phase prior to back-extraction of caprolactam into water to produce an aqueous caprolactam solution which undergoes final purification

by distillation. The lower ammonium sulphate-rich phase is also extracted with organic solvent to recover residual caprolactam from this phase. The lightly-loaded organic solvent from this secondary extraction is used as part of the solvent in the primary extraction of the caprolactam oil.

The organic solvent may be recycled continuously through the extraction process after purification by distillation to remove accumulated impurities.

DOMO Caproleuna GmbH use trichloroethylene (TCE) as the organic solvent of choice in this critical purification process.

## 2.1 *TECHNICAL FUNCTION*

This section describes the technical function of the TCE solvent in more detail, describing its physico-chemical properties and the key attributes required for optimal extraction of caprolactam from the caprolactam oil.

**Table 2.1** *Trichloroethylene*

Substance Description	Value
Formula	C <sub>2</sub> HCl <sub>3</sub>
Molecular Weight	131.4 g/mol
CAS-No.	79-01-6
EC-No.	201-167-4
REACH Registration Number	01-2119490731-36-0000
Boiling Point	110°C

**Table 2.2** *Classification according to Regulation (EC) No 1272/2008*

Property	Category	Hazard Phrase
Skin irritation	Category 2	H315 Causes skin irritation
Skin sensitization	Category 1	H317 May cause an allergic skin reaction.
Eye irritation	Category 2	H319 Causes serious eye irritation
Carcinogenicity	Category 1B	H350 May cause cancer.
Germ cell mutagenicity	Category 2	H341 Suspected of causing genetic defects.
Specific target organ toxicity - single exposure (Narcotic effects.) (Inhalation)	Category 3	H336 May cause drowsiness or dizziness.

Property	Category	Hazard Phrase
Chronic hazards to the aquatic environment	Category 3	H412 Harmful to aquatic life with long lasting effects.

**Table 2.3** *Classification according to Directive 67/548/EEC*

Risk Phrase	Description
R45	May cause cancer. Carcinogen category 2
R68	Possible risk of irreversible effects. Toxic for reproduction – category 3.
R36/38	Irritating to eyes and skin. Xi
R43	May cause sensitization by skin contact.
R67	Vapours may cause drowsiness and dizziness.
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

The required technical functions of the organic solvent in the recovery of caprolactam from caprolactam oil are identified in Table 2.4 (after Müller, 2013; Hampe, 1984).

**Table 2.4** *Required technical functions of an extractive solvent for caprolactam purification*

Technical function
<b>A. Specificity and loading</b>
Rapid and selective partition of the target solute, caprolactam, in both the primary (caprolactam oil) and secondary (ammonium sulphate phase) extraction processes
High selectivity and uptake capacity (loading) in primary and secondary extraction processes
<b>B. Operational practicality</b>
Sufficient density difference between the organic and aqueous phase to promote rapid separation
Low viscosity to assist solvent flow and fluid dynamics
Optimal surface tension to prevent emulsion formation (too low, small droplet formation) whilst maximizing droplet surface area for efficient phase transfer of the target solute (too high, large droplets)
Low or minimal solubility in the aqueous phase to reduce solvent loss and solute retention in the aqueous phase
Effective release of target solute on back extraction in a water phase with minimal carryover of organic solvent extracted impurities (e.g. cyclohexanone)

<b>Technical function</b>
Large difference in boiling points between organic solvent and target solute to prevent formation of azeotropes
Low or no corrosivity
Non-flammable liquid for operation in non-flammable areas and equipment to minimize operational risk
No negative safety or environmental impacts
<b>C. Solvent recovery</b>
Low boiling point in the range 90-110°C to minimize energy requirements for solvent recovery
Vapour pressure to minimize loss to ventilation systems and associated requirement for extensive abatement
Chemical and thermal stability to reduce solvent loss through degradation throughout process

Solvent selection will require a compromise in optimizing all of these technical and process requirements, especially in optimizing selectivity for caprolactam whilst maximizing the loading capacity of the organic solvent for caprolactam during the extraction process.

The following table summarizes the most important aspects of TCE for its technical function as a solvent for caprolactam synthesis.

**Table 2.5** *Key characteristics of TCE as an organic solvent in caprolactam extraction*

<b>Attribute</b>	<b>Value</b>
Extractive Efficiency Overall (Initial)	97% (56%)
Loading Capacity for Caprolactam (DOMO)	25% w/w in solvent for 50% w/w in water
Density	1.465g/ml
Boiling Point	87°C
Water Solubility	1.1g/l
Flammability	No
Viscosity	0.58 mPas
Vapour Pressure	99 hPa at 20°C

### **2.1.1** *Extractive efficiency, solvent loading capacity and selectivity*

The commercial production process uses counter-current continuous extraction. DOMO Caproleuna GmbH use a laboratory method for the characterization and comparison of organic solvents which simulates this

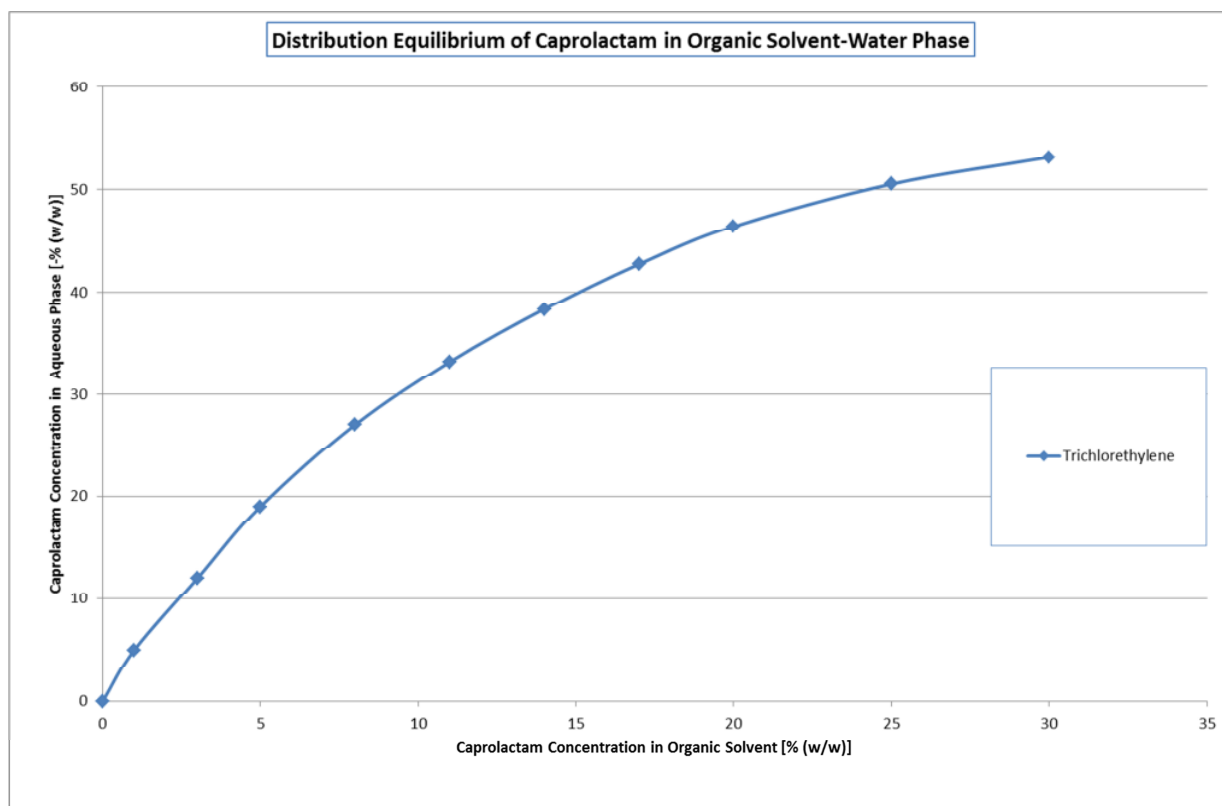
extraction process (Müller, 2013) but does not replicate the performance of the full scale industrial process. However, it allows direct comparison of solvent performance under controlled laboratory conditions.

The caprolactam oil (commercial production sample) is extracted with the solvent in a ten step sequential extraction process. After each step the solvent (caprolactam-containing TCE) is isolated whilst the oil is re-extracted with another aliquot of fresh TCE and the amount of caprolactam extracted into the solvent is determined by chromatographic methods (GC and HPLC). On completion, the solvents from the ten extraction steps are combined and the overall yield is determined and the results quoted as the percentage of caprolactam recovered by the complete extraction process (overall extractive efficiency) and percentage of caprolactam recovered in the first extraction step (initial extractive efficiency).

When TCE is used as the extractive solvent an overall efficiency of 97% is observed after ten extractive steps, with an initial extraction efficiency of 56%.

Figure 2.2 illustrates the distribution equilibria of caprolactam between mother liquor and trichloroethylene. The distribution curve shows that, at 30°C, caprolactam at an initial concentration of 50% w/w in the aqueous phase will be extracted to a final concentration of 25% w/w in the TCE organic phase. As will be discussed later, this distribution is not as favorable for other organic solvents, where the final caprolactam concentration in the organic phase is lower when extracted from the aqueous phase at an equivalent initial concentration.

Figure 2.2 *Caprolactam distribution equilibria in water and organic solvents (DOMO, 2013)*



TCE is soluble in water at a concentration of 1.1g/l, which is a suitably low value to minimize solvent loss to and caprolactam retention in the extracted caprolactam oil phase.

The selectivity of the solvent for caprolactam over other impurities and by-products from the synthesis reaction, such as 2-cyclohexen-1-one, aniline, cyclohexanone, is important in producing a final caprolactam of sufficient purity for subsequent polymerization. The development of the commercial extraction process has been optimized over the many years of operations to not only optimize overall yield but also to improve the purity profile of the caprolactam final product.

DOMO Caproleuna GmbH purchase a specially purified trichloroethylene and initial solvent purity is a key parameter contributing to final product quality.

Caprolactam-enriched trichloroethylene from the primary extraction of caprolactam oil is washed with water to remove any water-soluble impurities.

Laboratory simulation of this wash water step shows that 15% of the caprolactam in the TCE is lost to the wash water, although this level of loss is not observed on the full scale plant. Subsequent back-extraction into water transfers practically all the remaining caprolactam (96%) from the trichloroethylene phase, to the aqueous phase.

Under laboratory conditions the purity profile of the caprolactam extracted using TCE can be characterized and used for comparative purposes in testing different organic solvents. The table below shows the specifications on purity set by DOMO Caproleuna GmbH for the purified product for commercial production and the values achieved when using TCE in laboratory conditions.

**Table 2.6** *Caprolactam purity specification*

Analysis Method	Purity Criteria, Maximum value, DOMO	TCE as extractive solvent	Purpose
Extinction at 290 nm	0.05	0.011	Measure for UV-active substances such as aromatics and conjugated double-bonded compounds, such as benzene, aniline and 2-cyclohexen-1-one
Permanganate absorption number	5.0	2.3	Measure for oxidisable impurities. The higher the value the more permanganate is consumed meaning more impurity
Volatile Bases	0.05 meq/kg	0.018	Measures the amount of compound (impurities) that produce ammonia when NaOH <sub>(aq)</sub> is applied to the caprolactam
HAZEN-colour number	5.0	0.801	Measures the amount of impurities through absorption of light at 390 nm, i.e. increasing colour of the caprolactam product in solution indicates greater levels of light-absorbing impurities (aromatics, conjugated alkenes, etc)

The overall yield from using the TCE extraction route under the laboratory conditions (Müller, 2013) was between 45 – 50% of the total caprolactam in the caprolactam oil. This is the overall yield for the primary extraction with TCE, the wash stage, re-extraction with water and subsequent purification stages of solvent extraction and distillation. Although this is different to the yields



routinely observed from the large scale industrial conditions (yield in the industrial plant by DOMO Caproleuna GmbH is approximately 99%), it is useful as a comparator for this analysis of alternatives with other organic solvent systems, as discussed below.

The final caprolactam product does not contain any residual trichloroethylene. The lifecycle of trichloroethylene in its uses as an extractive solvent is therefore limited to its use on the DOMO Caproleuna GmbH site and the disposal of waste residues by off-site incineration.

### 2.1.2 *Operational Practicalities*

Rapid phase formation and separation, following intimate contact between the organic solvent and the caprolactam oil are key aspects of counter current extraction processes for efficient process operation. It has been postulated (Müller, 2013) that a density difference of at least 0.2 kg/l between the solvent and the caprolactam oil is required for rapid phase separation. The density of the caprolactam oil is 1.046 kg/l and that of the ammonium sulphate-rich aqueous phase is 1.24 kg/l. A TCE density of 1.46 kg/l achieves this criterion for both the primary and secondary extraction processes.

Where longer times are required for separation of organic and aqueous phases, because of a smaller density difference between the extractive solvent and the caprolactam oil, this will result in a slower throughput through the counter-current extraction columns, due to the need for longer contact time, or the requirement for larger capacity extraction columns.

The secondary solvent extraction from the high ionic aqueous environment in the ammonium sulphate phase means that the organic compounds are 'salted out' into the organic phase, i.e. they preferentially partition to the organic solvent rather than the highly ionic aqueous solvent (water). This aids the dissolution, separation and selectivity of caprolactam in the TCE and other organic solvents in this secondary solvent extraction procedure.

## 2.2 *PROCESS FUNCTION*

In addition to technical functions of solvent capacity and selectivity, there are a number of process functions that the extraction solvent has to satisfy in order to ensure that process operability, efficiency and economics are maintained and controlled.

The extraction solvent therefore should be

- Suitable for economic recovery and recycling through the process by distillation;
- Non-flammable, such that the extraction and solvent recovery equipment can be designed for and operated in a non-flammable production environment; and
- Totally contained to minimize risks of exposure to workers and to the environment.

2.2.1 Solvent Recovery

TCE is recovered in the DOMO Caproleuna GmbH process through a three-stage distillation process which maximizes TCE recovery and removal of undesirable residues for subsequent off-site disposal. TCE has a relatively low boiling point and the cost of TCE recycling can be estimated from the energy related costs provided by DOMO Caproleuna GmbH for the caprolactam production process.

Table 2.7 Economics of TCE Recovery at DOMO Caproleuna GmbH [2012]

Trichlorethylene			
Annual Solvent Use	tonnes/year	[REDACTED]	
	m <sup>3</sup> /year		
Solvent flow rate	m <sup>3</sup> /hour		
Solvent regeneration time	h		
Utility consumption		per hour	Annual cost (€)
Electricity	kW	[REDACTED]	
Low pressure steam	tonnes		
Medium pressure steam	tonnes		
Cooling water	m <sup>3</sup>		
Total Annual Utility Cost	€		
Annual Caprolactam Production Tonnage	tonnes		
Solvent utility cost per mt caprolactam produced	€/mt		
Note: Utility costs used; electricity [REDACTED]; low pressure steam [REDACTED] medium pressure steam [REDACTED] water, [REDACTED]			
Note 2: The caprolactam production cost is [REDACTED]			

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Any increase in this manufacturing cost will directly impact on the margin for this product and this is discussed further in section 4.2.5 where the process economics of the potential use of toluene are outlined.

### 2.2.2 *Process Safety*

Overall process safety and reduction of risk are key parameters in the operation of an industrial chemical production plant. TCE is not flammable and therefore TCE use in the production plant, even where the solvent transfer systems are all closed, does not require investment in additional plant design for fire and explosion protection in the equipment associated with the solvent extraction steps.

### 2.2.3 *Solvent Loss from the process*

The entire extraction process using trichloroethylene and the subsequent purification and recycling of TCE, is completely contained within the process equipment employed and TCE loss from the entire process is extremely low in relation to the rate of throughput of TCE. TCE loss can occur only at defined points in the process which are as follows:

1. Loss to exhaust vapours and atmosphere
2. Loss water wash streams
3. Loss to waste residues
4. Loss via in process degradation of trichloroethylene

Process losses to atmosphere and water wash streams total no more than 25 kg per annum. TCE loss to waste residues, which go for incineration, totals less than 8 metric tonnes per year.

However, in process degradation accounts for in excess of 99% of the total process loss from the process

#### 2.2.3.1 *Proposed mechanism of TCE degradation*

Trichloroethylene is known to be unstable to oxidation under normal storage conditions, resulting in the generation of low concentrations of condensation products upon prolonged storage, and epichlorohydrin is added to virgin TCE

as a stabilizer. The process of purification and recycling of TCE through this process removes this stabilizer. TCE is stable in aqueous environments and is extremely recalcitrant in natural aqueous environments under neutral conditions at 25°C.

However, the in-situ aqueous phase degradation of trichloroethylene (TCE) into carbon dioxide (CO<sub>2</sub>) and chloride (Cl<sup>-</sup>) has been reported to occur during the thermal treatment of contaminated subsurface environments (Knauss *et al.*, 2000), based on experimental results obtained from a completely water-filled, constant pressure, gold-walled reactor operated in the temperature range from 70 to 100°C (Knauss *et al.*, 1999). The only degradation products reported in these experiments were dissolved carbon dioxide and chloride. The US EPA recently published a review of the effect of thermal treatments on the chemical reactivity of trichloroethylene and summarised the literature on the thermal stability of TCE non-aqueous phase layers in industrial processes. These studies showed that, whilst the rate of degradation was not fast, at elevated temperatures the oxidation of TCE can occur.

The use of TCE in the caprolactam extraction process involves the recycling of process liquors containing dissolved trichloroethylene back to the Beckmann rearrangement process and it is proposed that the aqueous oxidation of a small fraction of TCE occurs during this process. The extent of the degradation is limited by the short time during the process cycle to which the TCE is exposed to conditions under which aqueous oxidation to carbon dioxide and chloride ions can occur. It is estimated that the annual turnover rate of TCE is in excess of 1,500,000 mt [REDACTED]

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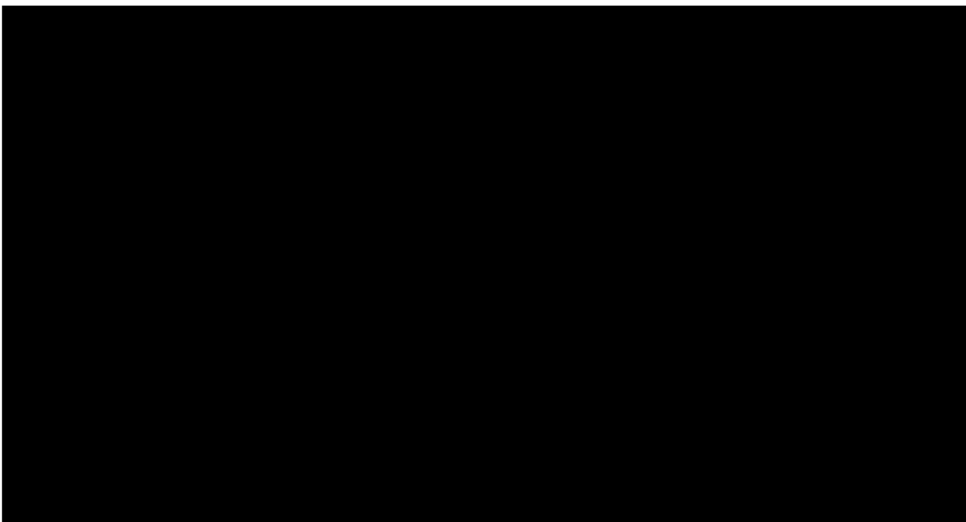
[REDACTED] Aqueous oxidation therefore only accounts for a very small fractional loss of TCE through degradation.

It is postulated that the degradation of TCE leads to the production of carbon dioxide and chloride ions alone. No other TCE degradation products have been identified in the TCE used in the extraction process. Carbon dioxide will either be vented from the process via the single air emission point or dissolved in process aqueous waste as bicarbonate. The chloride ion is retained within the system (in the TCE phase this has been directly measured) and is eventually transferred to the ammonium sulphate aqueous phase.

### 2.2.3.2 *Monitoring of chloride ions in production processes*

Chloride ion concentrations have been monitored in both the ammonium sulphate stream that is discharged from the caprolactam process and sent for

ammonium sulphate recovery and in the recovered ammonium sulphate product (DOMOGRAN®).



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These estimates of trichloroethylene loss due to oxidative degradation are of the same order as the actual purchased quantities of virgin trichloroethylene on an annual basis to make up the trichloroethylene inventory on plant. It is not known at present whether there are other potential sources of chloride ion in the various process streams that might account for some of the annual chloride load and not be attributable to TCE degradation.

### 3 IDENTIFICATION OF POSSIBLE ALTERNATIVES

#### 3.1 LIST OF POSSIBLE ALTERNATIVES

Caprolactam has been produced by the synthesis route described above for many years, during which time the industry has optimised the process and sought alternative solvents and technologies for the caprolactam extraction step.

Three solvents are used currently in commercial caprolactam synthesis: trichloroethylene, toluene and benzene.

Other solvents and solvent combinations have been researched but not implemented on a commercial scale (e.g. nitrobenzene, other chlorinated solvents, methylcyclohexane and solvent mixtures like n-heptane/1-heptanol, methylcyclohexane/1-octanol and n-heptane/1-octanol).

The following sections assess the technical characteristics of these solvent systems and compare both their technical and economic suitability as an alternative for TCE in this use.

So far as known all producers use one or more extraction steps to produce caprolactam.

#### 3.2 DESCRIPTION OF EFFORTS MADE TO IDENTIFY POSSIBLE ALTERNATIVES

##### 3.2.1 *Research and development*

DOMO has optimized the use of TCE in the extractive recovery of caprolactam over many years as part of a very cost competitive caprolactam manufacturing process to produce caprolactam in high yield and high purity.

DOMO has supported the following research:

**Table 3.1** *DOMO Internal Research on Optimisation of TCE extraction process*

Year	Title
1992	Reduction of the energy and raw material consumption for the manufacture of caprolactam by series connection of the re-extractors

Year	Title
	Tests regarding the use of SULZER packings for CL extraction (amongst others proposals, contract)
	Pilot tests on lactam oil extraction, re-extraction and AS lye extraction using steel and glass extractor (packings)
	Large-scale testing of lactam oil extraction, re-extraction, AS lye extraction and AS leach 7 extraction using SULZER packings
	CL balance extraction: Calculation of CL concentrations in water lactam K610 for all extraction levels using refraction and ultrasound. Conversion of CL concentrations in tri-lactam and water lactam from Mass % into g/l.
	Deinstallation of Sulzer-Packings: Equilibrium data CL-extraction, resonance oscillation system and other development studies, pulsation extraction (small-scale study using Bateman pilot extractor) data for one-line process in the lactam oil and re-extraction, values for average loading
1988	Design for the installation of a trial vibration extractor in the Caprolactam extraction unit (ITWV interim report 28/88 of 10.11.88)
	Balance calculations regarding the distribution of CL and impurities in the extraction
	Evaluation of the Effectiveness of the Sulzer AS extractor (Pos. 652a), root cause analysis, clarification of fluctuating caprolactam contents in the AS 5 solution
1999	Assessment of the high load condition at K 610 A in the month of October (1999)
	Installation extractor cascade K652: Reachability of CL content in the AS lye 5 (B 654) applying varying CL contents in the AS solution 4 (k 652 a)
2000	Investigation of the effectiveness of Raschig Super-Rings (No. 2) as filling material in washing tower K 604 B
2000	Evaluation of a cascade connection of extractors K 652a and K 652b
2000	Feasibility study regarding the product team definition FL 10/00 (replacement of the recirculation of the AS solution 5 within the oximation)
2000	Evaluation of large-scale test 31G02 AS extractor K 652a (2000: Final report dated 18.10.2000)
	Report regarding the effectiveness review of the rotary disc extractor pos. 652b at reduced rotation speed
2001	Report on the control of the Sulzer AS extractor K 652 a in the period of 09.01.2001 – 21.02.2001

Year	Title
2004	Modification of the three-level FVA to condensate pipelines DN 80
2005	Programme performance test of the process steps optimization to extraction of line B to determine hydraulic limit loads
2006	Results of the energy analysis CLP-3
2007	Laboratory and technical center tests on the AS 7 extraction
2009	Classification of trichloroethylene
2010	Analysis of large-scale AS 7 stripping over K 570
2010	Analysis performance run entire facility Caprolactam
2012	Investigations on the elimination of trichloroethylene traces from the "ammonium sulfate solution 5"

The research and development summarized in Table 3.1 defines the investment in the optimization of the caprolactam manufacturing process over the last twenty years, since the caprolactam manufacturing unit was acquired by the DOMO Group, to improve process and energy efficiency and process safety. This investment has resulted in a very high level of company proprietary knowledge of the safe and efficient use of TCE in the caprolactam extraction process. This has enabled the cost efficient large scale manufacture of caprolactam to be operated at the Leuna site with no known adverse impact arising from the use of and potential for exposure to TCE.

Additionally it should be noted that had under existing legislation referring to the use of chemicals (Chemical Agents Directive 98/24/EC –article 6 and Carcinogens Directive 2004/37/EC – article 4.1) and as transposed into German legislation by the Gefahrstoff-Verordnung (§ 6) each hazardous substance needs to undergo an evaluation for potential substitutes. DOMO documents this for trichloroethylene in a substitution evaluation according to the timing stipulated by the legislation every second year.

Hence had there been a suitable alternative solvent identified DOMO would have been obliged to switch to it already.



### 3.2.2 *Data searches*

Research focused on the identification of alternative solvent systems that may be technically viable as an option to the use of trichloroethylene and other commercially used solvents, toluene and benzene.

As defined in section 2 and in table 4.18, a suitable solvent system needs to combine a high capacity for caprolactam (to extract as much of the target solute as possible) with a low mutual solvent solubility with water (to mix as little with the caprolactam oil mother liquor) in order to optimize the extraction and purification of caprolactam. From a technological point of view, it is clear that if a solvent does not meet all of the selection criteria defined, then this substance cannot be regarded as a potential alternative to the current extraction solvent.

Due to both the commercial importance and historic nature of the caprolactam process, a literature review will identify many articles reporting the potential for improving the caprolactam manufacture and extraction process and the use of alternative solvent systems.

Many of these reports have described how the manufacturing process can be adjusted to obtain optimum two-phase liquid systems for separation of caprolactam from ammonium sulphate, such that the highest levels of caprolactam can be extracted preferentially into the organic solvent.

Research has also examined the purification of the raw caprolactam by other methodologies, for example via evaporation and distillation to reduce process energy consumption.

Table 3.1 summarises the publications that have been used in constructing this analysis of alternatives to trichloroethylene for the extractive purification of caprolactam from caprolactam oil.

Table 3.2

## Publication Summary

Year	Author	Title	Publication	English Title
2013	DOMO (Internal)	Stand der derzeitigen und zukünftigen Forschungsarbeiten zum Ersatz des Lösungsmittels Trichlorethen		State of the current and future research studies on the replacement of the solvent trichloroethylene
2013	Müller, R.	Auswahl und Bewertung alternativer Lösungsmittel für den Extraktionsprozess der Caprolactamherstellung	Aufgabenstellung für die Masterarbeit von Herrn R. Müller, Hochschule Merseburg, Germany	Selection and Assessment of alternative solvents for the extraction process of caprolactam production
2013	Dong-xuan <i>C. et al</i>	Liquid- liquid extraction of caprolactam from water using room temperature ionic liquids	Separation and Purification Technology, <b>104</b> , 263-267	
2012	Ritz J. <i>et al</i>	Caprolactam	Wiley-VCH Verlag GmbH	
2012	Guo, Cuili	Solubility of caprolactam in different organic solvents	Fluid Phase Equilibria, <b>312</b> , 9-15	
2010	Gong X. <i>et al</i>	Phase equilibrium calculations in mixtures containing caprolactam with a UNIFAC model	Chinese Journal of Chemical Engineering, <b>18(2)</b> , 286-291	
2008	Gong X. <i>et al</i>	Selection and evaluation of a new extractant for caprolactam extraction	Chinese Journal of Chemical Engineering, <b>16(6)</b> , 876-880	
2007	Gong X. <i>et al</i>	Distribution Coefficients of caprolactam and Methyl caprolactam Using Benzene or Toluene as Extractants: Experiments and Prediction	Chinese Journal of Chemical Engineering, <b>15(4)</b> , 463-467	
2007	Glazko, I.L. <i>et al</i>	Performance and selectivity of organic solvents in extraction of caprolactam from lactam oil	Russian Journal of Applied Chemistry, <b>80(6)</b> , 941 - 944	
2006	van Delden M.L. <i>et al</i>	Selection and evaluation of alternative solvents for	Separation and Purification	

		caprolactam extraction	Technology, <u>51</u> , 219-231	
2005	van Delden M.L	Caprolactam extraction in a pulsed disc and doughnut column with a benign mixed solvent	Thesis, University of Twente, Netherlands	
2004	Jianzhou Gui, Youquan Deng, Zhide Hua and Zhaolin Suna	A novel task-specific ionic liquid for Beckmann rearrangement: a simple and effective way for product separation	Tetrahedron Letters, <u>45</u> , 2681–2683	
2004	Chao-Hong, He	Optimization of the process for recovering caprolactam from wastewater in a pulsed-sieve-plate column using green design methodologies	Journal of Loss Prevention in the Process Industries, <u>17</u> , 195-204	
2003	van Bochove, G.H	Two- and three-Liquid Phase Equilibria in Industrial Mixed-Solvent Electrolyte Solutions	Technical University of Delft, Netherlands	
2002	Wittig, Roland	Experimentelle und theoretische Untersuchungen zur Erweiterung der Gruppenbeitragsmethoden UNIFAC und Modified UNIFAC (Dortmund)	Dissertation, University Oldenburg	Experimental and theoretical investigations for enlargement of group methods UNIFAC and modified UNIFAC
2002	van Bochove, G.H	Two- and three-Liquid Phase Equilibria in the system water + 2-heptanone + caprolactam + ammonium sulphate: experiments and modelling	Fluid Phase Equilibria, <u>194 – 197</u> , 1029-1044	

1999	van Bochove, G.H	Measurements of liquid-liquid of water + caprolactam + electrolyte + organic solvent system equilibria	Fluid Phase Equilibria, <u>158-160</u> , 939-947	
1999		BASF Caprolactam production	Ullmann's Encyclopedia of Industrial Chemistry, sixth edition, Wiley-VCH	
1997	Vanni, A. <i>et al</i>	Caprolactam production a comparirison of different layouts of the liquid- liquid extraction section	Chem. Eng. Technol., <u>20</u> , 445-454	
1985	Hampe, M.J.	Lösungsmittel-Auswahl bei der Flüssig/Flüssig-Extraktion unter physikalisch-chemischen Aspekten	Chem.-Ing.-Tech <u>57 (8)</u> , 669-681	Solvent selection in the liquid/liquid extraction under physico-chemical aspects
1981	Leuna-Werke (Internal report)	Phasengleichgewicht Trichlorethen/Caprolactam - Wasser/Caprolactam und Vorextraktion		Phase equilibrium trichlorethene/caprolactam-water/caprolactam and pre-extraction
1980	US EPA,	Caprolactam recovery from aqueous manufacturing streams	EPA-600/2-80-062	
1970	Leuna-Werke (Internal report)	Untersuchungen zur Verbesserung der Phasentrennung in der Lactamöl-Extraktion		Tests on the enhancement of phase separation during lactam oil extraction
1970	Leuna-Werke (Internal report)	Ermittlung einer optimalen Stoffführung in Drehscheibenextraktoren unter Berücksichtigung von Seitenströmen		Determination of optimal substance flow rates in the wheel extraction considering side flows
1969	Leuna-Werke (Internal report)	Versuche zur Extraktion von Lactamöl unter Verwendung von Trichlorethylen, Benzol und Toluol als Extraktionsmittel		Extraction tests for lactam oil using trichloroethylene, benzene and toluene as extraction agents
1960	Tettamanti,	Equilibria of the ternary system caprolactam /	Dep. Chem. Eng., Polyt. Uni. and	

	K. <i>et al</i>	water / organic solvent, in the liquid state	Research Inst. Of Ind. Org. Chem. and Plastics, Budapest	
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Both, Müller (2013) and van Delden (2006) investigated the use of alkane and alcohol mixtures as potential alternative extraction solvents, in comparison with other organic chlorinated and non-chlorinated solvents. This research showed that the caprolactam distribution ratio (uptake in the organic phase) increases

- with increasing mixed solvent polarity, as characterized by a more polar active group (eg ether, ester, ketone and alcohol);
- with decreasing carbon chain length of the polar solvent (C<sub>12</sub>-C<sub>6</sub>); or
- increasing the polar solvent fraction in the mixture (mixing an alcohol with an alkane).

Therefore, the inclusion of an alcohol in a mixed solvent increases caprolactam capacity through increased polarity. However, this is offset by the good mutual solubility of the alcohol in water, which prevents or reduces mixed solvent phase separation. Alkanes, on the other hand, have very low solubility with water but have low capacity for caprolactam due to low solvent polarity. Mixtures of the two solvents can be engineered to take up caprolactam through the polarity of the combined solvent but also minimise the mutual solvent solubility. The research showed that the optimal mixed solvent system for high caprolactam capacity, a low mutual solvent solubility and beneficial physical properties was 40% w/w alcohol in alkane. This research is discussed further in section 4.3.

Therefore, assessing the capability of alternative solvent systems has been the target of the caprolactam industry for many years, balancing the technical functional requirements of the solvent to produce high yield, good quality caprolactam against the practical process efficiency, safety and financial implications to maintain plant productivity, economic efficiency and maximise solvent recovery.

### 3.2.3 *Consultations*

DOMO Caproleuna GmbH is a member of the consortium which coordinates the REACH registration dossier of caprolactam but this did not require any discussion with regard to manufacturing methodologies. Any exchange of

process information between competitors is always claimed as business confidential information.

There is no specific information concerning extraction technology, solvent handling or energy consumption available from competitors. The three commercial solvents used are commonly known and have been used in industry standard extraction processes for many years.

However, for historic and geopolitical reasons caprolactam manufacturers are aware of which solvents are used by competitors. DOMO has consulted with other caprolactam manufacturers, who use trichloroethylene, concerning existing publicly available knowledge of potential alternative solvents.

This section compares the technical and process functions and hazards of other commercial (toluene and benzene) and non-commercial solvent systems with that of TCE for the extractive recovery of caprolactam.

Non-commercial solvents were selected from various solvent classes (alkanes, alcohols, glycols, amines, ketone, ether, aromatics, ester and chlorinated hydrocarbons) based on their appropriate physical and chemical properties.

- **Alkanes and alcohols:** Based on publicly available information it is known that mixtures of alcohols and alkanes have been tested for caprolactam extraction. Solvent mixtures were therefore evaluated for extractive performance using commercially produced caprolactam oil. For the results refer to section 4.4
- **Glycols:** the water solubility of glycols is generally too high for consideration as an alternative extraction solvent
- **Amines:** these are known to be soluble in water or to have high boiling point and can therefore be excluded as a potential alternative replacement solvent for TCE in caprolactam extraction. Moreover there is an additional risk of side reactions caused by the process conditions (low pH-value) which will lower product yield and purity.
- **Ketones:** excluded from further examination because of the existence of the carbonyl group in the molecule, which is highly reactive and can participate in unwanted side reactions with the caprolactam molecule.
- **Ethers:** extensive examination of the use of ethers was not carried out. The tendency for peroxide formation while handling ethers and the associated danger of explosion is well known.
- **Esters:** some esters are used as commercial solvents but despite having a loading capacity for caprolactam they are inappropriate as alternative solvents due to low density (< 0.9 g/ml), flammability and low chemical stability.
- **Short-chain chlorinated hydrocarbons:** these have been considered in searching for acceptable alternatives due to their similar physical properties and chemical stability to TCE. There are some chlorinated solvents with an acceptable a loading capacity for caprolactam (e.g. chloroform and dichloroethane). Unfortunately the phase separation

of chloroform and caprolactam oil is insufficient. Other kinds of chlorinated hydrocarbons are very toxic (tetrachloroethane), carcinogenic (1,2-dichloroethane) or suspected to be carcinogenic (trichloroethane, dichloromethane). Other short-chain chlorinated hydrocarbons excluded as potential substitutes by their low boiling point (< 60°C) and low density (< 1.3 g/ml).

- **Long-chain chlorinated hydrocarbons:** because of the dominating alkane character of these solvents they do not match the technical criteria required of an alternative solvent.
- **Aromatics:** Benzene and toluene from the group of aromatics have been considered because they are used commercially in the caprolactam extraction process (see below, chapter 4.1 and 4.2). Other aromatics, for instance xylene or nitrobenzene, are excluded from consideration because of their inappropriate physical properties.

## 4.1 *TOLUENE*

Toluene is a commonly used and widely available solvent used in many industrial extraction processes. It is used primarily due to its relatively low boiling point and good ability to partition organic compounds. Its properties, technical function and inherent risks are well known and thoroughly characterized. However toluene is flammable.

### 4.1.1 *Substance ID and properties*

Toluene is a clear liquid substance at room temperature. It is flammable with a boiling point of 110°C and an auto-ignition temperature of 535°C. It is less volatile than TCE, which has a boiling point of 87°C.

**Table 4.1** *Toluene*

Substance Description	Value
Formula	C <sub>7</sub> H <sub>8</sub>
Molecular Weight	92.14 g/mol
CAS-No.	108-88-3
EC-No.	203-625-9
Boiling Point	110°C



**Table 4.2**

***Classification according to Regulation (EC) No 1272/2008***

<b>Hazard Classification</b>	<b>Hazard Statement</b>
H225	Highly flammable liquid and vapour.
H304	May be fatal if swallowed and enters airways.
H315	Causes skin irritation.
H336	May cause drowsiness or dizziness.
H361d	Suspected of damaging the unborn child.
H373	May cause damage to organs through prolonged or repeated exposure.
IARC Group 3	Not classifiable as to its carcinogenicity to humans

The conclusions of the recent CoRAP evaluation of the toluene recommended that a review of the occupational exposure level be referred to the Scientific Committee on Occupational Exposure Limits (SCOEL) to take into account results from the EU RAR (2003) and determine whether there is a need to update the recommendation on an indicative OEL (IOEL) value for toluene.

In comparison with the inherent properties of TCE, although toluene is not carcinogenic it introduces other hazardous properties, principally flammability and reproductive toxicity, which can be considered to be of only marginally less risk than those presented by TCE itself, especially under conditions of strict control in a closed system that is used by DOMO Caproleuna GmbH in this process.

**4.1.2 Technical feasibility**

**Table 4.3**

***Key characteristics of toluene in comparison with TCE as an organic solvent in caprolactam extraction***

<b>Attribute</b>	<b>Toluene</b>	<b>TCE</b>
Extractive efficiency, Overall (Initial)	79% (20%)	97% (56%)
Loading capacity for caprolactam (DOMO)	8% w/w for 50% w/w in water	25% w/w
Density	0.865g/ml	1.465g/ml
Boiling Point	110°C	87°C
Water solubility	0.5g/l	1.1g/l

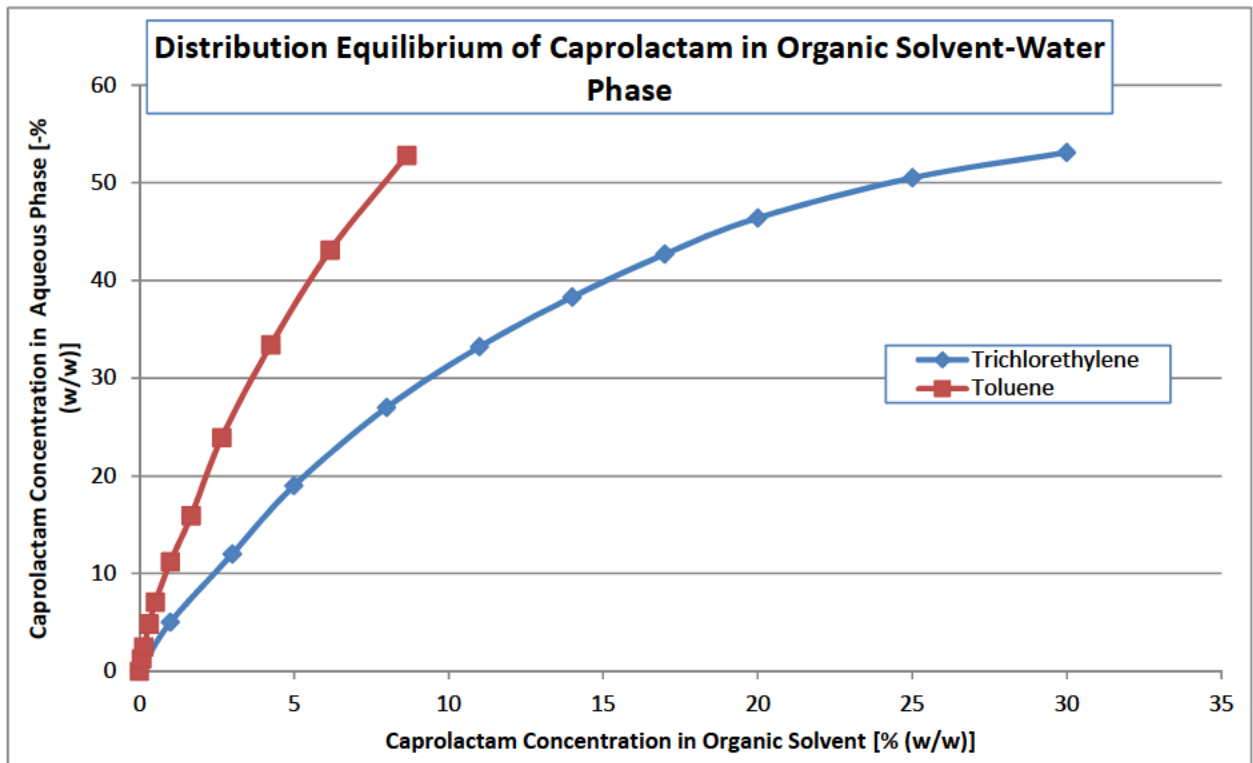
Attribute	Toluene	TCE
Flammability	Flammable	Non-flammable
Viscosity	0.6 mPas	0.58 mPas
Vapour pressure	29.1hPa at 20°C	99 hPa at 20°C

#### 4.1.2.1 *Extractive efficiency, solvent loading capacity and selectivity*

The laboratory comparison of the extractive efficiency of toluene demonstrates that the overall caprolactam capacity of toluene as an extractive solvent is about a third of that of TCE.

A comparison of solvent characteristics for distribution equilibria of caprolactam between water and a given organic solvent also demonstrates that, at 25°C, caprolactam is extracted to a final concentration 8% w/w in toluene from an initial concentration of 50% w/w in water, and this is three times lower than for trichloroethylene under comparable extractive conditions (Figure 4.1).

Figure 4.1 *Caprolactam distribution equilibria in water and organic solvents (DOMO, 2013)*



As toluene has one third of the caprolactam loading capacity in comparison with TCE, a solvent extraction process using this solvent will require the use of larger volumes to achieve the extraction of caprolactam from the same tonnage of caprolactam oil. This has significant implications for both capital investments in the production plant and on production costs, through increased energy requirements for solvent mobilization and recovery.

The density of toluene is closer to that of water than TCE is and as such it will require a longer time for separation of the two phases, resulting in a higher holdup of the two phases in the extraction system. The practical consequence of this is that larger diameter extraction columns are required to maintain the operational productivity of the production plant. It is calculated that an increase in extraction column diameter from 1.2m (using TCE) to a minimum of 3m would be required if toluene were to be used as the extractive solvent.

In addition, as toluene is less dense than water (whereas TCE is denser than water), the use of toluene as an extractive solvent would require reconfiguration of the solvent flow through extraction plant so that the solvent flows from the bottom to the top of the extraction columns. In the current production plant configuration TCE flows from the top to bottom, counter current to the caprolactam oil.

The water solubility of toluene is low compared to TCE (0.5g/l vs 1.1g/l), and is suitable to minimize solvent loss to and caprolactam retention in the extracted caprolactam oil phase.

Under laboratory simulation of the wash water step (Muller, 2013), more caprolactam is lost to the wash water when using toluene in comparison with TCE: 37% compared to 15%. This is due to

- the higher affinity caprolactam has for water when dissolved in toluene than when dissolved in TCE and that
- TCE has a higher capacity to retain the caprolactam.

Caprolactam will partition from toluene to water more readily than from TCE to water. This may reduce the overall yield of the extractive process. Müller (2013) found that the yield (caprolactam content) after the forward (organic) extraction and water wash stages was 82% when using TCE but only 50% when using toluene, as depicted in *Figure 4.2*. As stated before, these are laboratory conditions that are *modelling* full scale production for comparative

purpose rather than replicating actual full scale performance, but nonetheless are useful in indicating of the relative performance of the different solvents.

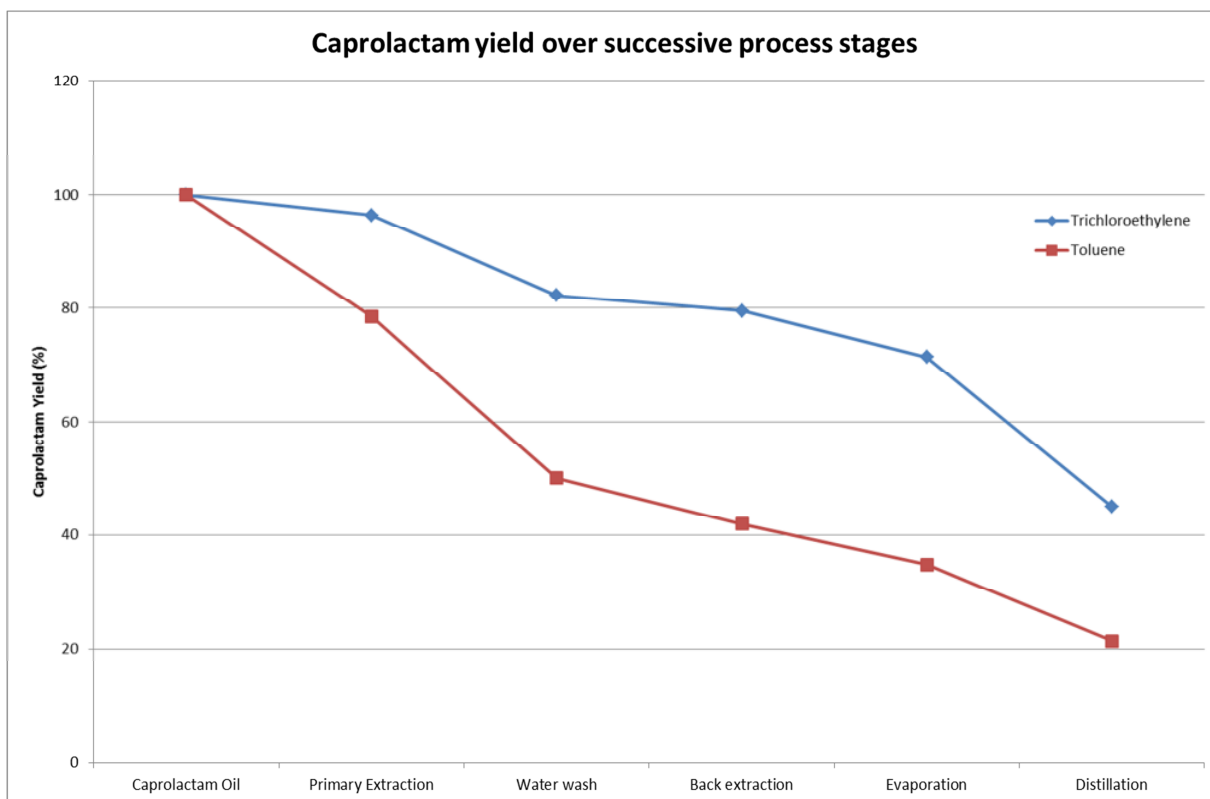


Figure 4.2 Caprolactam yield over successive process stages (Müller, 2013)

Under laboratory conditions the purity profile of the caprolactam extracted from a commercial sample of caprolactam oil using toluene as an extractive solvent is of similar quality to that from the analogous TCE extraction process and both samples conformed to the purity criteria set by DOMO (Müller).

Table 4.4 Caprolactam purity specification comparison

Analysis Method	Purity Criterion Maximum value, DOMO	Toluene as extractive solvent	TCE as extractive solvent
Extinction at 290 nm	0.05	0.02	0.011

Analysis Method	Purity Criterion Maximum value, DOMO	Toluene as extractive solvent	TCE as extractive solvent
Permanganate absorption number	5.0	2.8	2.3
Volatile Bases	0.05 meq/kg	n/a	0.018
HAZEN-colour number	5.0	1.001	0.801

#### 4.1.2.2

##### *Operational Practicalities*

Because of the lower extractive capacity of toluene for caprolactam from caprolactam oil, higher volumes of toluene will be required to maintain overall process intensity in terms of tonnes of caprolactam recovered in unit time. From the data presented above it can be estimated that three times the mass of toluene as compared to TCE, equivalent to fivefold increase in volume, will be required to maintain the current process intensity. The major impact of the increase in solvent volume will be:

- Higher energy costs for pumping increased volumes of solvent through the plant during the extraction process (see section 4.2.1).
- Higher energy costs for solvent recovery (see section 4.2.1).
- Capital investment to increase the size of the plant to accommodate higher solvent volumes.

The extraction plant would therefore need to be completely re-designed and constructed to accommodate this increase in volumetric capacity for the extraction and solvent recovery processes.

#### 4.1.2.3

##### *Process Function*

##### *Solvent Recovery*

Due to toluene's higher enthalpy of evaporation and higher boiling point, a difference of 23°C, there will be a higher energy requirement for solvent purification by distillation. In addition there will be additional energy consumption from an increase in pumping requirements derived from moving a large inventory of solvent through a reconfigured plant. Table 4.6 provides an estimate in the increase the overall production cost.

There will therefore be an increase in the overall production cost of caprolactam resulting from an increase in operational production costs and depreciation costs of the capital spend.

### *Process Safety*

The use of a flammable solvent will require plant and equipment upgrade for operation in a flammable environment in order to mitigate against this risk, even though the delivery system for the solvent is closed at all points, except where virgin solvent is delivered into the system. In addition, toluene has a similar health risk profile to TCE and offers no substantial reduction of risk from the inherent properties of the substance.

### *Solvent Loss from Process*

Although toluene has a lower vapor pressure than TCE, which will reduce the potential for evaporative loss to process exhaust air, its higher boiling point and enthalpy of evaporation will lead to higher energy costs in the recycling and purification of the solvent by distillation.

#### 4.1.2.4 *Conclusion*

Therefore, although toluene is an alternative solvent for the extractive recovery of caprolactam that is used commercially by other caprolactam manufacturers, it has several distinct disadvantages compared to trichloroethylene in the process operated by DOMO Caproleuna GmbH:

- Lower extractive capacity will require a significant increase in the solvent inventory, resulting in increased capital expenditure and operational costs.
- Increased risk through introduction of a flammable solvent and increased capital cost in upgrading a non-flammable to flammable zoning.
- No overall reduction in risk to human health or the environment from the inherent risk profile of this solvent.


So, although toluene is widely used as a solvent for commercial caprolactam extraction in other businesses, there are significant process and subsequent economic implications for DOMO Caproleuna GmbH in potentially making a switch to toluene with no benefit in terms of a reduction in health or environmental risk.

4.1.3 *Economic feasibility*

4.1.3.1 *Capital Costs*

An estimate of the capital investment required is presented in Table 4.5 and was calculated by detailed examination of the current capital replacement cost for equipment for the extraction and solvent recovery processes using TCE and then, where appropriate, applying an engineering cost scaling factor, based on chemical engineering experience at DOMO Caproleuna GmbH, for all capital equipment items that would require replacement in the event of toluene being the solvent of choice.

*Table 4.5 Capital Cost Estimate for Conversion of Caprolactam Plant to use Toluene as the extractive solvent*

Capital Item	Current Capital Investment cost, trichloroethylene as solvent, €k	Estimated Required Investment cost toluene as solvent, €k
Equipment - Section 44		
Equipment - Section 45		
Equipment - Section 46		
Equipment - Section 49 (toluene storage)		
Equipment - all sections		
Mounting apparatus		
Pipework		
Isolation		
Painting		
MSR		
Process Control System		
Electricity		
Civil / structural		
Engineering		
<b>Sub total</b>		
Contingency (10% of sub total)		
Work authorization (Eng. & Government costs) [1% of sub total + contingency]		

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Capital Item	Current Capital Investment cost, trichloroethylene as solvent, €k	Estimated Required Investment cost toluene as solvent, €k
Approvals (TUV, ...) [0.5% of sub total + contingency]		
Assembly insurance [1% of sub total + contingency]		
<b>Total cost</b>		

The switch from TCE to toluene would require substantial changes to the extraction section and interconnecting pipework, which lead to an estimated investment of more than €100 million based on an annual capacity of approximately 165,000 t. Such a high cost cannot be passed on to the customers nor be absorbed by DOMO. This estimated investment cost is equivalent to the total investment made by DOMO in the period 2008 to 2012 and would erode significantly the cost competitiveness of the DOMO caprolactam production process. Without any return on investment it is unlikely that this would be sanctioned by the DOMO board and shareholders.

#### 4.1.3.2 Operational costs

Due to the lower loading capacity, the extraction process will require a greater amount of toluene, estimated as an increase by a factor of three by mass and by a factor of five by volume, to process the same tonnages of caprolactam and maintain the same process throughput.

Table 4.6 Comparative economics of TCE and Toluene Recovery [2012]

		TCE		Toluene	
Annual Solvent Use	tonnes/year	[Redacted]			
	m <sup>3</sup> /year				
Solvent flow rate	m <sup>3</sup> /hour				
Solvent regeneration time	h	[Redacted]			
Utility consumption		per hour	Annual cost (€)	per hour	Annual cost (€)
Electricity	kW	[Redacted]			
Low pressure steam	tonnes	[Redacted]			
Medium pressure steam	tonnes	[Redacted]			

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		TCE	Toluene
Cooling water	m <sup>3</sup>		
Total Annual Utility Cost	€		
Annual Caprolactam Production Tonnage	tonnes		
Solvent utility cost per mt caprolactam produced	€/mt		

Note 1: Utility costs used; electricity, [redacted] low pressure steam, [redacted] medium pressure steam [redacted] water [redacted]

Note 2: The caprolactam production cost is [redacted]

These estimated costs include provision for the increased energy requirement for pumping large volumes of solvent through the extraction plant as detailed in Table 4.7.

**Table 4.7** Breakdown of energy requirements in the caprolactam extraction process (2012, based on an annual capacity of 165,000 t)

Energy Requirement	Primary Caprolactam Oil Extraction	Secondary ammonium sulphate phase extraction	Solvent recovery (existing process)	Solvent recovery (upgraded or alternative process)	Total (existing)	Total (upgraded or alternative process)
<b>Trichlorethylene as solvent</b>						
electric energy (kWh)						
low pressure steam (t/h)						
medium pressure steam (t/h)						
cooling water (m <sup>3</sup> /h)						
<b>Toluene as solvent</b>						
electric energy (kWh)						
low pressure steam (t/h)						
medium pressure steam (t/h)						
cooling water (m <sup>3</sup> /h)						

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### *Carbon dioxide emissions*

The additional energy demand for toluene recovery will also contribute an annual increase in carbon dioxide generation of an estimated 68,384 tonnes per annum from the mixed energy sources detailed in table 4.6 and 4.7.

#### *4.1.3.3 Impact of switching to toluene on the cost competitive position of DOMO Caproleuna GmbH in the global caprolactam market*

Substitution of TCE with toluene would therefore result in an overall investment cost of €100 million in addition to an increase in annual operating costs and depreciation cost of €20 million, leading to a total cost penalty of €300 million for a period of 10 years. This would result in a period of 5 years of no available cash flow for other investments or maintenance activities depending on the achievable financial and commercial results in this period.

DOMO believes that it would be practically impossible to find a bank to finance such an investment where there is no prospect of any return at all and which would, in addition, jeopardize the current very cost competitive global market position of DOMO as a European caprolactam producer. If DOMO was placed in a position where the company was required to replace TCE with toluene as an extractive solvent, this financial burden would catalyse the decision to close the whole DOMO manufacturing plant. This in turn would leave the shortfall in European production capacity open to Chinese caprolactam manufacturers to export their material to Europe without knowing the circumstances of their production processes in China with respect to environment and social responsibility (see also SEA sections 3.4.2, 3.4.3 and 3.4.4).

The resulting estimated increase cost of caprolactam production is shown in Table 4.8.

**Table 4.8** *Estimated impact of toluene substitution on caprolactam manufacturing cost*

<b>Cost item</b>	<b>Cost</b>
Capital cost to adapt plant for toluene	€ 100,000,000
Annual capital depreciation cost (discounted at 4% over 10 years)	€ 12,329,094

Cost item	Cost
Annual increase in energy cost	€ 8,122,740
Total increased annual production cost	€ 20,451,834
Total production of caprolactam (mt)	164,322

Substitution of TCE with toluene would therefore result in a significant erosion of the manufacturing cost margin, thus eliminating DOMO's cost competitive position and its viability as a caprolactam manufacturer. These additional costs cannot be passed on to the customers or absorbed by DOMO.

#### **4.1.4 *Reduction of overall risk due to transition to the alternative***

Given the current level of containment there is no overall lowering of exposure risk from switching to this solvent, even though it is slightly less volatile.

#### **4.1.5 *Availability***

Toluene is a commonly used solvent and feedstock in industrial synthesis and as such is commercially available in required tonnages and is REACH registered.

#### **4.1.6 *Conclusion on suitability and availability for Toluene***

There is no overall reduction in risk to human health or to the environment from the potential switch from TCE to toluene as the current process in a closed system with solvent recovery and recycling, resulting in very low emissions to the working environment. Toluene introduces alternative health and process safety risks (reproductive toxicity, flammability) in place of carcinogenicity. The high capital investment cost to effect the transition and increased operational cost would bring no worker health or environmental benefits for a process that is operated under strictly controlled conditions. The increase in production cost would significantly erode the cost competitive position of DOMO Caproleuna GmbH in the global caprolactam market.

## 4.2 *BENZENE*

Benzene is a commonly used and widely available solvent used in many industrial extraction processes. Despite its flammability it finds favor due to its relatively low boiling point and its good ability to partition organic compounds.

### 4.2.1 *Substance ID and properties*

Benzene is a clear liquid substance at room temperature. It is flammable with a boiling point of 80°C and an auto-ignition temperature of 562°C. It is slightly more volatile than TCE.

**Table 4.9** *Benzene*

Substance Description	Value
Formula	C <sub>6</sub> H <sub>6</sub>
Molecular Weight	78.11 g/mol
CAS-No.	71-43-2
EC-No.	200-753-7
REACH No.	01-2119447106-44-0000
Boiling Point	80°C

**Table 4.10** *Classification according to Regulation (EC) No 1272/2008*

Hazard Classification	Hazard Phrase
H225	Highly flammable liquid and vapour.
H304	May be fatal if swallowed and enters airways.
H315	Causes skin irritation.
H319	Causes serious eye irritation.
H340	May cause genetic defects.
H350	May cause cancer.
H372	Causes damage to organs through prolonged or repeated exposure.
IARC Group 1	Carcinogenic to humans.

In comparison with the inherent properties of TCE, benzene is carcinogenic and introduces other hazardous properties, principally flammability. It therefore offers no inherent decrease in risk through its use as an alternative to TCE and so will only be considered in brief detail as it is used commercially in the extraction of caprolactam.

#### 4.2.2 *Technical feasibility*

**Table 4.11** *Comparative characteristics of benzene and TCE in the extraction of caprolactam*

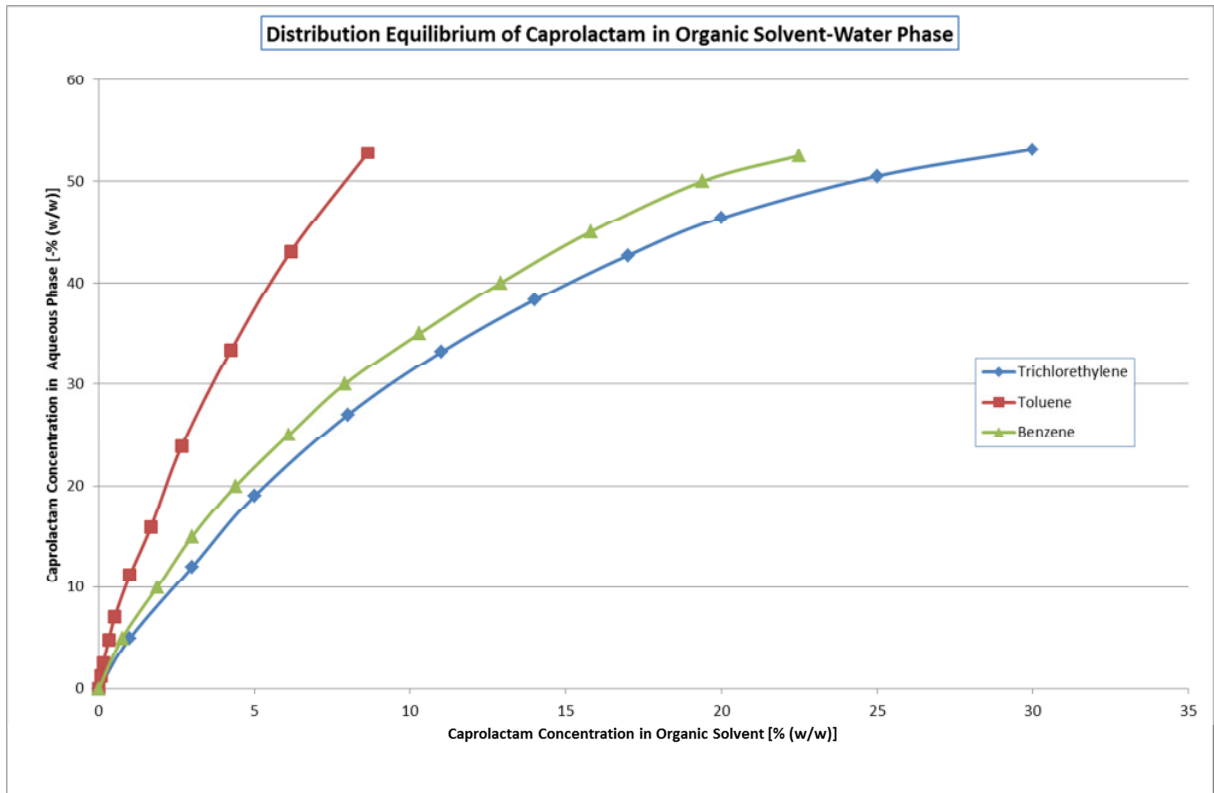
<b>Attribute</b>	<b>Benzene</b>	<b>TCE</b>
Extractive efficiency, Overall (Initial)	n/a (45%)	97% (56%)
Loading capacity for caprolactam (DOMO)	19% w/w for 50% w/w in water	25% w/w
Density	0.88g/ml	1.465g/ml
Boiling Point	80°C	87°C
Water solubility	1.8g/l	1.1g/l
Flammability	Yes	No
Viscosity	0.66 mPas	0.58 mPas
Vapour pressure	100hPa at 20°C	99 hPa at 20°C

##### 4.2.2.1 *Extractive efficiency, solvent loading capacity and selectivity*

Benzene has a capacity of 45% for caprolactam on initial extraction at 25°C, compared to 56% using TCE when tested under laboratory conditions. Figure 4.4 illustrates this slight reduction of benzene capacity for caprolactam to 77.6% of that for TCE under equivalent conditions.

Figure 4.3

Caprolactam distribution equilibria in water and organic solvents (DOMO, 2013)



Therefore, benzene and TCE have a similar capacity for the extraction of caprolactam from caprolactam oil. However, as with toluene, more caprolactam will be lost in the wash water step in comparison with TCE, thus potentially reducing the potential overall yield. In the back-extraction step practically all caprolactam will transfer into the aqueous phase leaving organic impurities behind, in a similar manner to TCE and toluene. The purity profile of caprolactam produced using benzene as the extractive solvent will therefore be within the required production specification and similar in quality to the final product derived from either TCE or toluene solvent extractions.

Furthermore, benzene also has a lower density than water which means that the extraction plant must be reconfigured to reverse the solvent flow in the counter-current extraction process, incurring increased capital and, potentially operational costs.

Low mutual solvent solubility of benzene in water 1.8g/l, compared to that of TCE, will cause slightly more water to be taken into the organic phase with the caprolactam in the forward extraction. However, this is not expected to cause operational problems in emulsion formation and phase separation.

Benzene has a slightly lower boiling point of 80°C than TCE, but a higher enthalpy of evaporation. Higher energy input per volume of solvent will therefore be required for solvent recovery which, combined with a lower capacity for caprolactam therefore a higher volumetric requirement for benzene, results in increased operational production costs.

As extractive solvent benzene can fulfil the technical functions for the extractive recovery of caprolactam but offers no benefit in the reduction of overall risk from its use.

#### **4.2.3 *Economic feasibility***

As described in section 2 for toluene, a change of extraction solvent from TCE to benzene would require significant capital expenditure to reconfigure the plant to accommodate a flammable solvent used at greater volumetric throughput and overall solvent inventory.

As there is

- no overall reduction in risk to worker health or the environment in using benzene in comparison with TCE (both are carcinogenic),
- a slightly lower capacity for caprolactam resulting in increased operational and capital costs to accommodate higher inventory volumes and rates of use and hence increased costs,

benzene as an alternative solvent is discounted from further detailed analysis.

#### **4.2.4 *Reduction of overall risk due to transition to the alternative***

There would be no reduction in overall risk in moving from TCE to benzene as the substance is of similar/increased risk for carcinogenicity as well as being flammable. Furthermore, benzene has a lower capacity for caprolactam than TCE which would require greater volumes of solvent and hence increased costs for extraction and recovery plant.

#### 4.2.5 *Availability*

Benzene is a commonly used solvent and feedstock in industrial synthesis and as such is commercially available in required tonnages. It has been fully registered under REACH.

#### 4.2.6 *Conclusion on suitability and availability for benzene*

A move to benzene from TCE will not result in any risk reduction as both solvents have similar carcinogenicity profiles and comparable characteristics in terms of technical function as an extractive solvent.

#### 4.3 *N-HEPTANE / 1-HEPTANOL*

Significant research has been conducted on identifying suitable solvent systems for caprolactam extraction that are alternatives to toluene, benzene and TCE.

This section summarises the work of Müller (2013) and van Delden (2006) who investigated the use of alkane and alcohol mixtures as potential alternatives, in research sponsored by DSM and DOMO Caproleuna GmbH respectively.

In summary, the research has shown that a 40% w/w mixture of 1-heptanol in n-heptane is the optimal balance of the properties required technical properties for an extractive solvent and so has been included here as a viable alternative.

#### 4.3.1 *Substance ID and properties*

##### *n-Heptane*

Heptane is a clear liquid substance at room temperature. It is flammable with a boiling point of 98°C and an auto-ignition temperature of 223°C. It is slightly more volatile than TCE.

**Table 4.12** *Heptane*

<b>Substance Description</b>	<b>Value</b>
Formula	C <sub>7</sub> H <sub>16</sub>
Molecular Weight	100.20 g/mol
CAS-No.	142-82-5



Substance Description	Value
EC-No.	205-563-8
Boiling Point	98°C
Density	0.684g/ml
Water Solubility	insoluble

**Table 4.13** *Classification according to Regulation (EC) 1272/2008*

Hazard Classification	Hazard Statement
H225	Highly flammable liquid and vapour.
H304	May be fatal if swallowed and enters airways.
H315	Causes skin irritation.
H336	May cause drowsiness or dizziness.
H410	Very toxic to aquatic life with long lasting effects.

The substance may be toxic by inhalation, causing damage to the peripheral nervous system, upper respiratory tract, skin and central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage. The solvent is not carcinogenic or mutagenic.

*1-Heptanol*

1-Heptanol is a clear liquid substance at room temperature. It is flammable but does not ignite readily, but heptanol vapour burns more readily. It has a boiling point of 176°C and so is far less volatile than TCE.

**Table 4.14** *1-heptanol*

Substance Description	Value
Formula	C <sub>7</sub> H <sub>16</sub> O
Molecular Weight	116.2 g/mol
CAS-No.	111-70-6
EC-No.	203-897-9
Boiling Point	176°C
Density	0.822g/ml

Substance Description	Value
Water Solubility	1.63g/l

**Table 4.15** *Classification according to Regulation (EC) No 1272/2008*

Hazard Classification	Hazard Statement
H319	Causes serious eye irritation

#### 4.3.2 *Technical feasibility*

**Table 4.16** *Key characteristics of a mixed solvent system in comparison with TCE*

Attribute	n-Heptane/1-Heptanol (60/40)	TCE
Extractive efficiency, Overall (Initial)	100% (5%)	97% (56%)
Loading capacity for caprolactam (DOMO)	n/a	25% w/w
Density	0.74g/ml (weighted)	1.465g/ml
Boiling Point <sup>b</sup>	113	87°C
Water solubility	0.65g/l (40% of 1.63g/l)	1.1g/l
Flammability	Yes	No
Viscosity <sup>b</sup>	1,15 mPas	0.58 mPas
Vapour pressure <sup>b</sup>	< 80 hPa	99 hPa at 20°C

Müller (2013) tested the n-heptane/1-heptanol mixture under laboratory conditions for comparison with TCE and toluene. The caprolactam extraction profile in such mixed solvent systems is different from the characteristics for both TCE and toluene. The first extraction step in the laboratory ten step protocol returns a low comparative yield of caprolactam whereas subsequent extraction steps return higher comparative yields.

This phenomenon is attributed to a proportion of the alcohol dissolving into the caprolactam oil (through H-bonding between alcohol hydroxyl groups and water molecules) and therefore not being available as an extractive solvent for caprolactam out of the oil and into the mixed solvent in the earlier extraction steps. Once the oil is saturated with the alcohol however, in subsequent extraction 1-heptanol remains in the extraction mixed solvent and

hence the partition of caprolactam into the mixed solvent increases. In the laboratory after ten extraction steps all of the caprolactam has been extracted from the oil.

The alcohol/alkane mixed solvent also shows a lower selectivity for caprolactam than TCE. Although the mixed solvent takes up all 100% caprolactam, it also co-extracts impurities such as 2-cyclohexen-1-one and cyclohexanone. Therefore, the mixed solvent has a lower selectivity than TCE for caprolactam.

The calculated density of the mixed solvent is more than 0.2g/ml lower than water and hence should allow for ready separation of the phases. However, the mixed solvent is less dense than water and its potential use would require a reconfiguration of the extraction plant to reverse the direction of flow through the extraction columns.

As observed with all laboratory tested solvent systems, the use of a wash water step results in a loss of some of the caprolactam from the extraction solvent to the wash water. In the case of the mixed solvent this is greater (26%) than the caprolactam loss when using TCE (15%), again demonstrating higher affinity of TCE for caprolactam compared with other organic solvent systems. After the primary solvent extraction and water wash stages, 74% of the caprolactam remains in the mixed solvent compared to 74% when using TCE.

Practically all the caprolactam (94%) back-extracted from the mixed solvent into the water phase in the final back-extraction and the mixed solvent perform slightly better than TCE by holding onto more aniline impurity, but does releases more cyclohexanone impurity.

The final purity profile of caprolactam product derived from a mixed solvent system is within specification thresholds for product purity.

**Table 4.17** *Caprolactam, comparative purity specification*

Analysis Method	Purity Criterion Maximum value, DOMO	Heptane/Heptanol as extractive solvent	TCE as extractive solvent
Extinction at 290 nm	0.05	0.02	0.011
Permanganate absorption number	5.0	3.7	2.3
Volatile Bases	0.05 meq/kg	0.015	0.018

Analysis Method	Purity Criterion Maximum value, DOMO	Heptane/Heptanol as extractive solvent	TCE as extractive solvent
HAZEN-colour number	5.0	1.873	0.801

Under laboratory conditions, an extractive process using the mixed solvent produces a final caprolactam yield of 40%, compared to a yield of 45% using TCE, after a ten step extraction, washing, back-extraction and purification.

However the mixed solvent shows quite different extraction characteristics and it is not known how these would translate onto the full scale counter-current extraction system and the potential consequences for solvent volumetric flow and inventory.

It is speculated that untested equipment modification would be required, especially for the primary extraction step from caprolactam oil.

The most problematic hurdle to overcome in the use of a mixed solvent for caprolactam extraction is, however, in the recovery and recycling of the solvent mixture. An entirely new recovery process would need to be designed because n-heptane is a low boiling solvent, n-heptanol a high boiling liquid, with the boiling points of water and impurities in between. Different distillation columns will therefore be needed to recover liquids as well as additional storage and process equipment to store the substances separately after recovery and then mix in the correct proportions for subsequent use as an extractive mixed solvent. In addition, the chemical stability of the mixed solvent has not been fully determined. As yet under production conditions n-heptanol might undergo side reactions in order to form by-products such as olefins or ethers and furthermore it might also react with caprolactam to reduce overall yield.

Research has therefore shown that the mixed solvent (heptane/heptanol) system performed well in comparison with TCE with regard to the technical functions identified for the extraction of caprolactam from caprolactam oil and the removal impurities to achieve an acceptable final product purity specification. Individually, the solvents do not perform well in this regard whereas in combination in a mixed solvent a high capacity for the partition of caprolactam is achieved, and a two-phase system with quick phase separation suitable for counter current extraction is created. Based on a high caprolactam loading capacity, a low mutual solvent solubility and beneficial physical properties a mixed solvent of 40% (w/w) 1-heptanol in n-heptane was shown,

from laboratory scale evaluation, to be the most viable replacement solvent for toluene or TCE. Furthermore, caprolactam is extracted at an appropriate quality and at comparable process intensity to that achieved with the use of the conventional solvents. Nonetheless, mixed solvents systems with solvent recovery have not been implemented or piloted on a large commercial scale.

However a mixed solvent increases the complexity of solvent recovery, the alcohol and alkane needing to be recovered separately in sufficient purity for subsequent mixed solvent formulation. This will require increased distillation capacity and concomitant operational costs.

#### **4.3.3 *Economic feasibility***

As with any switch to a different solvent system, there will be capital investment costs for installations of new plant and increased operating costs associated with solvent recovery and re-use. The costs of implementing such as solvent extraction system have not been further estimated but are envisaged to be greater than the costs presented in section 4.1 for toluene, primarily due to the additional requirements for handling (unloading, storing and mixing) two solvents and for the subsequent more complex solvent separation and recovery system.

#### **4.3.4 *Reduction of overall risk due to transition to the alternative***

Switching to a mixed solvent alkane / alcohol system would introduce a solvent combination of lower toxicity profile than TCE but would introduce an additional flammability risk. The solvent system has been shown, at laboratory scale, to demonstrate the correct technical functionality to recover caprolactam to the required purity specification at acceptable process intensity. However, the economics of the recovery and recycling of a mixed solvent system and the impact this would have on the overall caprolactam production cost is unknown at this point in time. Capital investment in the plant would be required to handle solvent mixing and upgrade the plant to hazardous area operation.

In conclusion, there would be reduced risk from toxicity properties of the mixed solvent but an increased risk of flammability.

#### **4.3.5 *Availability***

Both of the solvents are commercially available in the required tonnages to supply DOMO Caproleuna GmbH as both have been registered under the

REACH Regulation to a cumulative annual tonnage greater than 1,000 metric tonnes per annum.

#### 4.3.6 *Conclusion on suitability and availability for heptane/heptanol*

Using mixed solvent such as n-heptane/1-heptanol, reduces the toxicity profile but introduces a flammability risk. Whilst the system satisfies some of the technical functions for an extractive solvent for caprolactam extraction for caprolactam oil, the system has not been piloted at larger scale to determine the unknown process design considerations regarding the overall efficiency and performance of counter current extraction and the costs of solvent recovery. It is therefore not a suitable or available alternative to the current use of TCE. Using a mixed solvent increases the potential investment cost compared with toluene by far more than €100 million. Again these costs are unacceptable and cannot be passed on to the customers nor be absorbed by DOMO.

#### 4.4 *SUITABILITY OF OTHER ORGANIC SOLVENTS*

An alternative solvent for the caprolactam extraction process has to undergo strong intermolecular interactions with the target solute, caprolactam, in order to effect dissolution in the solvent. In addition the solvent must have the ability to form a two phase system in a water/caprolactam/solvent system in the presence of high concentration of ammonium sulphate.

This can be achieved by using a solvent with polar functional groups (ether, ester, ketone and alcohol), by a decreasing carbon chain length of the polar solvent (C<sub>12</sub>-C<sub>6</sub>) or by increasing the polar solvent fraction in a solvent i.e. n-heptane/1-heptanol. From the table below it is concluded that there is not a suitable solvent for caprolactam extraction available which would be able to replace the TCE in the DOMO caprolactam process.

Table 4.18 Summary of Comparison of Potential Solvents for the Extraction of Caprolactam from Caprolactam Oil

Solvent Name	CAS No	EC No	BP	Density	Vapour Pressure	Water Solubility	Viscosity	Extraction Efficiency	Caprolactam Loading	Final Purity	Flammability	Comment
			°C	g/ml	hPa @ 20°C	g/l	mPas	%	%			
Trichloroethylene	79-01-6	201-167-4	87	1.465	99	1.1	0.58	97	25	2.3	Non-flammable	Optimum combination of properties
Toluene	108-88-3	203-625-9	110	0.865	29.1	0.5	0.6	79	8	2.8	Flammable	Flammable. Low loading capacity and low density would require complete re-engineering of extraction plant. Higher solvent requirement and higher boiling point would increase cost of solvent recovery
Benzene	71-43-2	200-753-7	80	0.88	100	1.8	0.66	n/a	19	n/a	Flammable	Flammable. Carcinogenic. Low density would require re-engineering of extraction plant
Mixed solvent (heptane:heptanol)	142-82-5 /111-70-6	205-563-8 /203-897-9	113	0.74	80	0.65	1.15	100	3.7	3.7	Flammable	Laboratory evaluation only. Flammable. Low loading capacity and low density would require complete re-engineering of extraction plant. Recovery of mixed solvent would be complex.
Heptane	142-82-5	205-563-8	98	0.684	69	0.003	0.438	n/a	< 1	n/a	Flammable	Flammable. Low density would require re-engineering of extraction plant.
Methylcyclohexane	108-87-2	203-624-3	100.9	0.769	61.8	11.014	0.679	n/a	< 1	n/a	Flammable	Low density would require re-engineering of extraction plant. High solubility in water.
Heptanol	111-70-6	203-897-9	176	0.822	0.7	1.63	7.3	n/a	See comment	n/a	Non-flammable	No two phase formation. Low density would require re-engineering of extraction plant. High solubility in water. High boiling point would increase cost of solvent recovery.

Solvent Name	CAS No	EC No	BP	Density	Vapour Pressure	Water Solubility	Viscosity	Extraction Efficiency	Caprolactam Loading	Final Purity	Flammability	Comment
Octanol	111-87-5	203-917-6	194	0.828	76 (@ 38°C)	0.107	4.62	n/a	See comment	n/a	Non-flammable	No two phase formation. Low density would require re-engineering of extraction plant. High boiling point would increase cost of solvent recovery.
cis-3-hexenol	928-96-1	213-192-8	154	0.848	2.26	19.3	1.357	n/a	See comment	n/a	Flammable	No two phase formation. Flammable. Low density would require re-engineering of extraction plant. High solubility in water. High boiling point would increase cost of solvent recovery.
Tetrachloroethene	127-18-4	204-825-9	121	1.61	25	0.15	0.844	n/a	< 1	n/a	Non-flammable	High boiling point would increase cost of solvent recovery. Carcinogenic properties.
Chloroform	67-66-3	200-663-8	62	1.48	211	8.7	0.57	n/a	40 See comment	n/a	Non-flammable	Very poor phase separation. High solubility in water. Carcinogenic and reprotox properties.
Xylene	106-42-3	203-396-5	138.4	0.857	11.67	0.156	0.603	n/a	n/a	n/a	Flammable	Flammable. Low density would require re-engineering of extraction plant. High boiling point would increase cost of solvent recovery.
Nitrobenzene	98-95-3	202-716-0	210.8	1.2	0.2	1.9	2.03	n/a	13	n/a	Non-flammable	High boiling point would increase cost of solvent recovery. Higher solubility in water. Carcinogenic and reprotox properties.
n-Butyl acetate	123-86-4	204-658-1	126	0.881	11	10	0.73	91	14	n/a	Flammable	Flammable. Low density would require re-engineering of extraction plant. High solubility in water. High boiling point would increase cost of solvent recovery.
iso-Butyl acetate	110-19-0	203-745-1	118	0.87	20	53	0.7	85	13.5	n/a	Flammable	Flammable. Low density would require re-engineering of extraction plant. High solubility in water. High boiling point would increase cost of solvent recovery.
tert.-Butyl acetate	540-88-5	204-658-1	97	0.86	41	1	0.74	71	11	n/a	Flammable	Flammable. Low density would require re-engineering of extraction plant. Low Caprolactam loading and low extraction



Solvent Name	CAS No	EC No	BP	Density	Vapour Pressure	Water Solubility	Viscosity	Extraction Efficiency	Caprolactam Loading	Final Purity	Flammability	Comment
Mixed solvent (methylcyclohexane:octanol)	108-87-2/ 111-87-5	203-624-3/ 203-917-6	n/a	n/a	n/a	n/a	n/a	98	33	3.9	Non-flammable	efficiency.  Complicated solvent recovery. Low density would require re-engineering of extraction plant
<i>Condition for selection of potential alternative</i>			>70<100	>1.3	<100	<1.1		>75	>12.5	<5	Non-flammable	
See below for explanation			A	B	C	D		E	F	G	H	

n/a = not available

A Highlighted cells indicate solvent BP may be too high for efficient solvent recovery

B Highlighted cell indicate that solvent density will require re-engineering of counter-current extraction columns

C Highlighted cells indicate solvent vapour pressure may lead to increased solvent loss

D Highlighted cells indicate that solvent water solubility is too high for application

E Highlighted cells indicate total extraction efficiency, based on DOMO laboratory methodology, may lead to longer contact times for the extraction process

F Highlighted cells indicate a loading capacity, determined from test extraction of 50% (w/w) caprolactam in water, that will require at least double the solvent inventory for the same production intensity

G Highlighted cells indicate extractive solvents that did not produce a final quality specification of caprolactam based on organic impurities as measured by permanganate number

H Highlighted cells indicate solvents that are flammable

## **OVERALL CONCLUSIONS ON SUITABILITY AND AVAILABILITY OF POSSIBLE ALTERNATIVES FOR USE**

All the potential solvents examined in this analysis are commercially available. However, there are technical feasibility and practical engineering issues to consider when assessing their suitability. None of the known alternatives can be used as a drop-in substitution.

In comparison with the other solvents used for commercial caprolactam recovery, toluene and benzene, TCE has a far greater loading capacity and selectivity to produce a caprolactam of higher quality. The increased loading capacity and inherent physico-chemical properties of TCE results in a more efficient solvent recovery and recycling. This means that a smaller plant footprint is required to achieve the same overall caprolactam tonnage output.

Although toluene is not a carcinogen, it is nonetheless flammable and is also hazardous to health. Toluene has a lower caprolactam capacity which results in increased energy consumption for solvent recovery to achieve similar process intensity and productivity as TCE. A switch to toluene as an extractive solvent would require high capital expenditure to install new plant of increased volumetric capacity and increased operational costs to recover and recycle the solvent. As there is no reduction in risk to human health or the environment due to the comprehensive risk management measures employed by DOMO Caproleuna GmbH, there is no overall advantage in the introduction of toluene as an alternative extraction solvent. This would impose a significant economic burden without leading to any risk reduction.

Benzene is a carcinogenic substance and there is no benefit in further consideration of this alternative as there is no reduced inherent hazard. Furthermore, benzene is also flammable and does not satisfy the technical function criteria as well TCE. As such benzene can be excluded as a potential alternative extraction solvent which would decrease risk to human health and to the environment in this specific use.

The study of mixed solvent systems, in particular alkane/alkanol mixtures, shows some potential for caprolactam recovery, with a lower solvent toxicity profile and comparable technical functionality. However, the practicalities of engineering a system based on such a mixed solvent have still to be evaluated and a detailed cost analysis undertaken to compare the additional capital investment and operational costs that would be incurred, due to increased energy requirements for mixed solvent recovery. However, it is anticipated that the investment required would be even higher than that estimated for the alternative use of toluene.

In conclusion, whilst an alternative solvent such as toluene is technically feasible, the current caprolactam purification plant would have to be extensively reconfigured to accommodate with much larger volumes and throughput, with potentially longer mixing times and higher temperatures of distillation whilst introducing the additional risk of flammability. All of these factors would significantly increase the operational costs of caprolactam production and erode the competitive position of DOMO Caproleuna GmbH in the global caprolactam market. Hence, none of the currently known alternatives are economically feasible.

The use of TCE by DOMO Caproleuna GmbH is very strictly controlled and rigorously contained in an industrial setting. There is no TCE present in the final product caprolactam and the life cycle is therefore limited to on-site use.

Trichloroethylene is considered the optimal solvent for caprolactam purification from caprolactam oil in the process operated by DOMO Caproleuna GmbH from both a technical and operational perspective due to the combination of high caprolactam loading capacity, selectivity for caprolactam and physicochemical properties that determine its effective performance characteristics in counter current extraction and solvent recovery processes.