Chemical

LIST Technology for the Recovery of Toluene Diisocyanate from Distillation Residue

Author: Dr. G. Raouzeos

LIST AG develops and industrializes advanced and customized solutions for the processing of viscous, sticky and crust-forming products.

The range of developed and implemented processes covers, among others, plants for the thermal treatment of "difficult" hazardous industrial residues, with effective recovery of solvents. The concept of the plants is based on a single step direct (contact) evaporation/drying process. No addition or recycle of any dry materials is necessary. The operating units are of closed design.

In the mid seventies, LIST developed and industrialized a continuous process for the recovery of toluene diisocyanate (further TDI) from distillation residue (see reference list in Appendix A). The process, which will be highlighted in this document, ensures the maximum recovery of TDI. The final residue is transformed into a non-toxic (neutral) and easy to handle solid/granular material. It can be either land filled, if this is allowed, or used as energy source (incineration). The recovered TDI is finally rectified in the purification stage of the production process.

INTRODUCTION

The production process of TDI, a component widely used in the production of polyurethane, yields substantial quantities of distillation residues containing anything from 30% - 50% by weight free TDI.

Considerable effort had been put into developing a commercial method allowing the complete recovery of free TDI from the distillation residue. It was soon realized that recovering TDI from the distillation residue specialized processing technologies are necessary.

In the following are highlighted the product and process requirements, the features of the process technologies, and last but not least the LIST process solution.

PRODUCT AND PROCESS REQUIREMENTS

During the TDI separation by evaporation, the liquid distillation residue passes through a rubbery, viscous, pasty phase with a strong tendency to foam. When the TDI content is below 17%, the residue solidifies and forms a crust. During the solidification and the build-up of the crust a severe risk exists to block the processing equipment. Due to the toxicity of TDI high level of containment must be ensured. The recovery of TDI by means of evaporation and drying should avoid uncontrolled thermal decomposition reactions.

PROCESS TECHNOLOGIES

The features of the processing technologies are: Rugged construction. High torque to overcome the viscous phase. Large vapor disengagement volume. Effective foam breaking action. Good self-cleaning of the heat exchange surfaces from the crust. Efficient "breaking" effect of the solidified residue. Enclosed, contained construction. Continuous operation. Vacuum operation. Narrow residence time distribution.

REVIEW OF PROCESSES

Several processes were tested in the past aiming the recovery of TDI from the distillation residue. A concise description follows:

- Concentration of the distillation residue in a stirred-tank vessel by evaporation under vacuum. Starting with a distillation residue containing 50% by weight free TDI, a final TDI

content of 30% by weight can be attained. Further concentration is not feasible due to the increase of the viscosity and the danger of solidification of the rather concentrated residue.

The disadvantages of this process are the tremendous loss of TDI (approx. 430 kg of TDI per ton of dry residue), the handling and disposal of the concentrated residue (odor, toxicity).

- Processing of the distillation residue by liquid-liquid extraction is an expensive process from the investment and operating costs point of view. It was not industrially implemented.

- Concentration of the distillation residue by means of thin film evaporation under vacuum. Staring with a distillation residue containing 50% by weight free TDI, a final TDI content of 20% by weight can be reached. Further concentration is not possible due to solidification of the concentrated residue in the process chamber of the thin film evaporator.

  The disadvantages of the above process are the high losses of TDI (250 kg of TDI per ton of dry residue), the handling and the disposal of the concentrated residue (odor, toxicity).

Applying the LIST Process Solution it is possible to recover TDI from the distillation residue down to a final content of less than 0.5% by weight. The process solution is based on the LIST Twin Shaft Processing Technology. The recovery is effected by evaporation/drying under vacuum. The final residue is an odorless, non toxic granular solid. It can be disposed or it can be incinerated for power generation. There are substantial economic advantages over alternative processes, as evaporation/drying takes place in a continuously operating plant with low energy and labor costs.

TECHNICAL FEATURES OF THE LIST TWIN SHAFT PROCESSING TECHNOLOGY FOR TDI RECOVERY

The LIST Twin Shaft Processing Technology is characterized by the two parallel inter-meshing agitator shafts rotating in a horizontal housing of a roughly figure-of-eight cross section (Fig. 1).

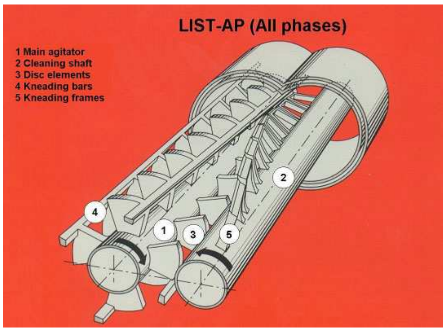


Fig. 1: Technical Features of the LIST Twin Shaft Processing Technology

The main agitator carries disk elements with kneading bars. The cleaning shaft is fitted with kneading frames that mesh with, and clean, the main agitators disk elements and bars. Intermeshing of the two sets of elements generates an intensive mixing/kneading action and effective self-cleaning. The arrangement of the kneading bars, frames, and disk elements is designed to provide a gradual forward conveyance of product, coupled with intensive lateral intermixing.

The shell housing, agitator shafts, and disk elements are heated. The heat exchange surface is very large in relation to the volume. The intensive mixing and kneading action, coupled with the self-cleaning of the heat exchange surface, combines to break up baked-on crusts, agglomerates and lumps, a major requirement for the TDI process. This ensures a high rate of product surface renewal for both heat and vapor transfer.

The kneading and agitation forces are high. To handle the required power,

these units operate with agitator shaft speeds between 10 and 30 rpm, and maximum available torques as high as $250 \cdot 10^3$ Nm. A spiral arrangement of the kneading elements imparts regular axial conveying, even at the highly viscous, pasty phase of TDI/residue mass in the process chamber. The LIST Twin Shaft Processing Technology is easily adaptable to changing feed rates or composition. This ensures high operational flexibility even under extreme circumstances.

The LIST Twin Shaft Processing Technology operates at fill levels in the range of 60 - 80% of total. That leaves adequate free volume for vapor disengagement. This is an important technical feature taking into account that the initial free TDI content in the distillation residue stream could be as high as 70% by weight, and that the process takes place under vacuum.

The final product is a free-flowing granular material. The average fill level in the unit is controlled by the height of an adjustable weir plate at discharge. Unlike screw type processing units, the axial conveying rate is independent of agitator speed, making it possible to select the rotation for optimal heat transfer, residence time, and minimizing attrition.

The disk elements do not affect the forward conveying function, but prevent back-mixing, enabling the processing of liquid feed stock directly through to a solid free-flowing material without recycling of dry product.

SCALE OF OPERATION

The application of LIST Twin Shaft Processing Technology for the recovery of TDI from distillation residue is considered when the annual production capacity is at least 10'000 tons. Figure 2 shows the processing capacity and flexibility of a LIST recovery unit with an annual recovery capacity in the range of 4'400 to 9'600 tons TDI.

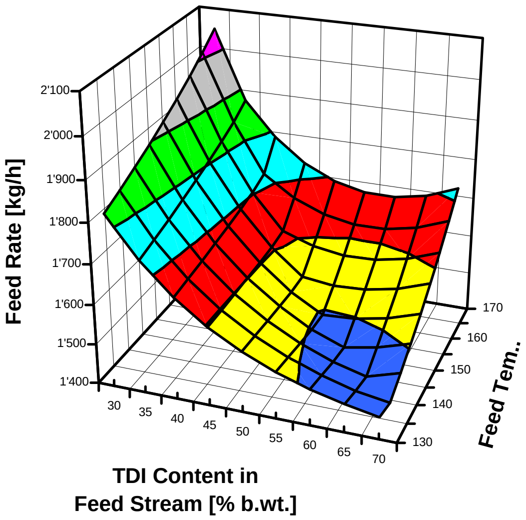


Fig. 2 : Processing Capacity and Flexibility

TDI RECOVERY APPLYING THE LIST TWIN SHAFT PROCESSING TECHNOLOGY

The annexed process flow diagram (Annex I, Fig. 3) shows the LIST process for the recovery of TDI from distillation residue.

Feed System

The distillation residue stream is continuously supplied from the bottom of the distillation column to the feed tank (Pos. 1). It functions as a feed tank. This tank levels out any fluctuations of the distillation residue feed stream that could happen up stream of the TDI recovery unit.
The supply rate of the distillation residue stream is controlled such that the level of the feed material in the feed tank is kept low and constant. In order to avoid evaporation and to prevent moisture penetrating into the feed tank, the feed tank is blanketed with N_2 sweep stream.

The feed tank is jacketed and heated by thermal oil. The temperature of the thermal oil is set such that the

temperature of the feed material in the feed tank should be the same as the temperature of the distillation residue in the bottom of the distillation column upstream to the feed tank. The control of the hold-up and of the heating temperature contribute to prevent thermal decomposition of the feed material. It is known that thermal decomposition of the feed material leads to the formation of solid tar particles as well as to the increase of the viscosity of the feed stream. The presence of the solid tar particles could eventually clog the feed line including the flash valve.

The bottom of the feed tank provides two individual feed lines. Each feed line is equipped with the following items:
The supply on/off valve on the bottom of the feed tank .
The purge TDI on/off valve. Purge TDI would be supplied to the feed line whenever it is suspected that the feed line is fouled by tar deposits, or the flash valve is clogged from tar deposits, or both. Purge TDI would also be supplied to the feed line whenever a regular shut-down for maintenance or for any other reason is executed. Washing the feed line(-s) by TDI it ensures that the feed line is clean from deposits and ready for the next feed operation.
The feed pump (Pos. 2A/B). The feed pump is double jacketed for being heated by thermal oil. The temperature of the thermal oil is the same as the one applied for heating the feed tank.

- Two flow transmitters are installed upstream respectively downstream to the flash valve (Pos. 3A/B). The flow transmitters measure and control the feed rate of the distillation residue stream to the Twin Shaft CONTI evaporator/dryer (Pos. 4).
- The flash valve (Pos. 3A/B) is automatically operated through the signal delivered from the flow transmitter to the actuator of the flash valve. Three distinct functions are fulfilled from the flash valve:
  1. It is a feed component
  2. It is a regulating feed valve
  3. It is a pressure regulating valve

There is always one feed line in operation and one feed line in stand-by mode. The stand-by feed line is clean and empty of feed material, but it is kept heated.

Drying Unit

The strongly motorized LIST Twin Shaft CONTI evaporator/dryer (Pos. 4) is suitable for the continuous vacuum evaporation/drying of sticky, crust forming residues. While the contained solvent(-s) or light boiling component(-s) would be evaporated, such residues would typically go through a pasty intermediate stage. Upon nearly completion of the evaporation of the light component the residue would finally turn into a free flowing/granular solid. It is apparent that during evaporation with subsequent drying in a single stage, several phase changes take place. The specific design of the Twin Shaft CONTI evaporator/dryer allows the effective processing of such feed material, and ensures maximum recovery of valuable components contained in the feed stream.
The effectiveness and efficiency of the Twin Shaft CONTI evaporator/dryer is attributed, but not limited, to its fully heated design, and its self cleaning characteristics. The casings and both shafts are of double jacket design. They are simultaneously heated by thermal oil of 240°C to 250°C. The thermal energy required to cover the latent heat of vaporization of the light component(-s) is mainly provided by indirect heat transfer, i.e., contact evaporation/drying. A lesser part is covered by dissipation energy. This is created from the friction of the product in the process chamber of the Twin Shaft CONTI evaporator/dryer with his static and rotating metallic surfaces, and is provided by the electric drive.

The distillation residue stream is usually available at a temperature of 140-150 °C. Occasionally higher feed temperatures apply (160-170°C). The operating pressure in the LIST Twin

Shaft CONTI evaporator/dryer is 25 mbar abs. range. Under these operating conditions it is possible that a flash evaporation takes place when the distillation residue stream enters the process chamber of the LIST Twin Shaft CONTI evaporator/dryer. Further TDI evaporation and subsequent drying take place along the length of the LIST Twin Shaft CONTI. The relatively low vacuum maintains the boiling temperature of the light component, in the present application TDI, as low as required in order to prevent extensive polymerization phenomena within the process chamber of the Twin Shaft CONTI evaporator/dryer.

During the course of the evaporation/drying process, the consistency of the distillation residue changes from liquid, through a highly viscous, paste phase to a final free flowing granular residual material. This change of phases is shown in Figure 4.

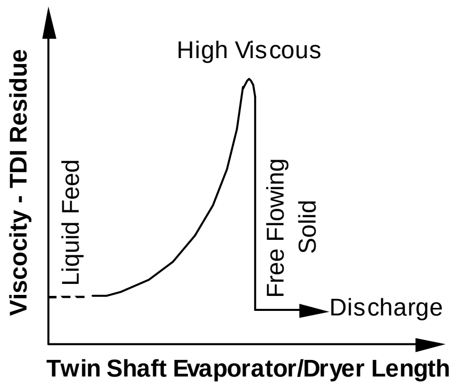


Fig. 4 : Change of phases of the feed material during processing

The TDI vapors are withdrawn through the heated vapor dome (Pos. 5). Due to the free volume available in the process chamber of the evaporator/dryer and the adequately designed vapor dome the vapor velocity is low. Hence, the risk of droplets and solid residue entrainment is minimized.

The TDI vapors are condensed in the spray condenser (Pos. 6). Condensation is accomplished by liquid TDI, which is recycled and accordingly tempered. The circulation pump (Pos. 7) of the TDI condensate is of centrifugal type. Tempering of TDI condensation stream take place in a shell and tube heat exchanger (Pos. 8). The cooling medium in the heat exchanger is water. The design of the spray condenser is such that it ensures washing of entrained fines of the solid residue. It also minimizes the risk of entrainment of TDI droplets to the primary vacuum station (Pos. 9).

The condensed TDI is partly discharged from the spray condenser and recycled for its final purification back to an upstream distillation unit of the TDI plant. The TDI discharge is controlled by a level controller positioned on the knockout drum of the spray condenser.

Discharge Unit

The final free flowing granular residue, remaining after the TDI evaporation (TDI content less than or equal to 0.5% by weight), is continuously discharged into a vacuum tight lock system.

The discharge unit consists of the following items:

- The LIST-SB buffer vessel (Pos. 10);
- The LIST-AV bottom discharge valve to the buffer vessel (Pos. 11);
- The LIST-SB lock vessel (Pos. 12);
- The LIST-AV bottom discharge valve to the lock vessel (Pos.13);
- The LIST-BF filter to the lock vessel (Pos. 14);
- The secondary vacuum pump (Pos. 15A/B).

The buffer and lock vessels are agitated and are cooled. The bottom discharge valves are vacuum tight and are pneumatically driven.

The discharge sequence of the final dry residue is a time dependent operation. The filling and the emptying sequence is described below:

Step 1:
The final dry residue is discharged by gravity from the LIST Twin Shaft CONTI evaporator/ dryer in to the buffer vessel (Pos. 10). This vessel operates at the same vacuum as the evaporator/dryer. The bottom discharge valve is shut. The residue is cooled.

Step 2:
After a certain time, the discharge valve of the buffer vessel (Pos. 11) opens and the residue flows by gravity into the lock vessel (Pos. 12). During this operation, the lock vessel (Pos. 12) is under the same vacuum as the rest of the system.

Step 3:
The discharge valve (Pos. 11) of the buffer vessel (Pos. 10) closes.

Step 4:
After a certain cooling time, the lock vessel is vented to atmospheric pressure with Nitrogen. Upon completion of the venting cycle its discharge valve (Pos. 13) opens. The cooled free flowing residue is discharged into a container or onto a conveying system.

Step 5:
The discharge valve (Pos. 13) of the lock vessel closes, and the lock vessel is evacuated by means of a secondary vacuum pump (Pos. 14) down to the operating pressure of the LIST Twin Shaft CONTI evaporator/dryer. The system is ready for the next discharge cycle.

PERFORMANCE

Overall material balances with respect to TDI recovery were performed on industrial plants. The measured TDI recovery is practically 100%.

It has been observed that a decomposition reaction takes place in the process chamber of the LIST Twin Shaft CONTI evaporator/dryer during the evaporation of TDI from the distillation residue. During this reaction, the oligomers contained in the distillation residue are decomposed generating CO_2. This gas is withdrawn from the system by the primary vacuum pump station.

The amount of recovered TDI depends on the capacity of the production plant as well as the amount of the distillation residue. Figure 5 shows the range of the annual recovery. Measurements performed on various industrial plants have shown that the recovered TDI amount lies in the range of ±10% of the nominal plant capacity. Considering the rather attractive sales price of TDI it has been calculated that the investment costs for a LIST TDI recovery unit can be paid back in more or less one year.

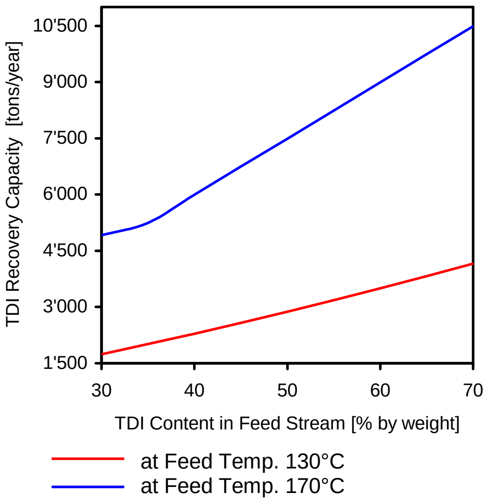


Fig. 5 : Range of Annual TDI Recovery

The flexibility of the LIST TDI recovery units ranges from 40% to 100% of the nominal processing capacity. Extreme reductions of the capacities lower than 40% of the nominal can also be handled.

BENEFITS OF THE LIST PROCESS
They can be summarized as follows:

- Reliable, industrially proven and low maintenance technology
- Closed design and TDI containment, environmental friendly operation

- Processing of the changing consistency of distillation residue in a continuous mode of operation
- High flexibility with respect to capacity and composition of the distillation residue
- One-step process, without addition or recycling of dry material
- Delivery of non toxic easy to handle final residue

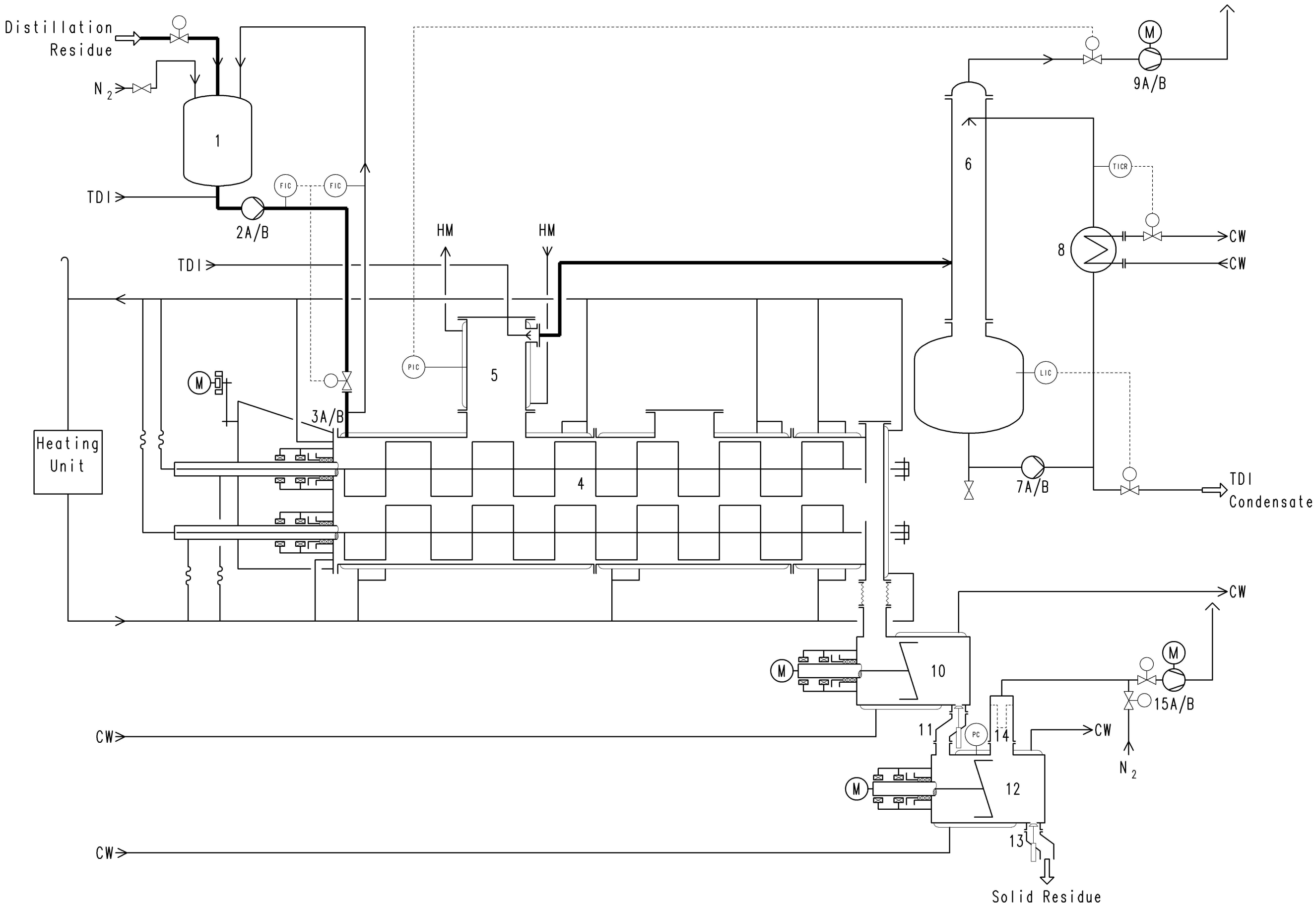
LIST SERVICES

LIST's expertise in the field of TDI recovery from distillation residue contributes to the development of customized plants in a close professional co-operation with the customer.

The LIST Services Comprise:

- Project definition in co-operation with the client
- Process concept outlining in co-operation with the client
- Preliminary investment costs proposal bases on principal key process equipment
- Binding investment costs proposal
- Project realization management, definition of responsibilities between client and LIST
- Project execution, detailed equipment engineering
- Basic engineering
- Manufacturing, procurement and delivery of key process equipment and ancillaries
- Training of operators and maintenance personal of the client
- Support during the installation of the process equipment and ancillaries
- Final inspection of the installation
- Mechanical start-up
- Process start-up
- Guarantee run and optimization of the operation
- Life Cycle Management Program comprising:
    1. Scheduled maintenance meetings
    2. Planned inspection and maintenance
    3. Planned overhaul
    4. Upgrades

Annex I


Distillation
Residue
N 2
1
TDI
FIC
FIC
2A/B
HM
HM
TDI
PIC
5
M
3A/B
Heating
Unit
4
6
TICR
8
CW
CW
M
9A/B
LIC
7A/B
TDI
Condensate
CW
M
10
M
15A/B
11
PC
14
CW
N 2
M
12
13
CW
CW
Solid Residue

For service please contact:

- Europe and South America
  Phone +41 61 815 30 30
- North America
  Phone +1 704 423 54 78
- Asia
  Phone +65 63 38 78 76
- Rest of World
  Phone +41 61 815 30 30

LIST AG
CH-4422 Arisdorf
Switzerland

Phone +41 61 815 30 00
Fax +41 61 815 30 01

www.list.ch
info@list.ch

LIST USA INC.
1629 Cross Beam Drive
Charlotte, NC 28217
USA

Phone +1 704 423 54 78
Fax +1 704 423 02 10

www.list.us
info@list.us

LIST AG
(SINGAPORE BRANCH)
122 Middle Road
#06-03 Midlink Plaza
SGP-Singapore 188973

Phone +65 63 38 78 76
Fax +65 63 38 37 71

www.list.sg
info@list.sg

We develop and industrialize advanced and customized solutions for processing of viscous, sticky and crust forming products for the polymer, chemical, fiber, food and environmental industries.