Chemical Polyester Recycling
Challenges and Hurdles to enter Industrial Scale

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1. Current status of chemical polyester recycling at industrial scale

Definition of chemical polyester recycling:
- Chemical recycling of polyethylene terephthalate are processes where the PET polymer chain is destructed by the impact of glycol (MEG) causing glycolysis, methanol causing methanolysis or water causing hydrolysis. After intensive purification polyester oligomers or the monomers MEG, DMT or PTA are received which are re-used to produce polyester products again applying state of the art polycondensation processes.

The following general processes of chemical polyester recycling are available:

1. Glycolysis
   \[ \text{PET} + \text{monoethylenglycol (MEG)} \rightarrow \text{Depending on molar ratio PET:MEG the resulting products are oligomers [Tm < 250^\circ C] or 2(2-hydroxyethyl) terephthalate (BEHT) [Tm 106 – 108^\circ C]} \]

2. Methanolysis
   \[ \text{PET} + \text{methanol} \rightarrow \text{Dimethylterephthalate (DMT) [Tm = 141,6^\circ C], DMT could be further destructed by water like DMT + Water \rightarrow \text{PTA} + \text{methanol [see also USP 7,462,649 or 6,472,557]} \]

3. Hydrolysis
   \[ \text{PET} + \text{H2O} \rightarrow \text{Terphthalic acid (TA) further purified terephthalic acid PTA [no melting behaviour]} \]

All three described base processes are applied currently to chemical polyester recycling at industry scale.

Potential market size for chemical polyester recycling

- The total market size of polyester produced for fiber, film and bottles was in 2008 about 53 Mio t per annum.
- The distribution across these three main applications was about 60% fiber and textile, about 31 % bottle and packaging resins and about 9% film and other applications.
- Looking at the related market figures of the recycling we find that assuming in 2008 about 5,5 Mio t/a bottle flakes has been collected the recycling proportion was related to bottle and packaging resins about 35%, related to the total polyester volume only about 10%.
- One portion of the recycled polyester market which is not statistically captures properly is the re-use of PET bottle flakes, re-granulate and external or internal production waste as partial feed material to polyester production lines for bottle or textile.
- The polyester industry is processing its in-house waste increasingly by direct recycling which is providing an increase of recycling production know how.
- Polyester fiber and filament waste especially sourced from used textiles, which is the main portion of the totally produced polyester fiber and filament is suffering from lack of recycling processes.
- Till today the only public known industrial size used PET textile recycling is operated by the Teijin-Patagonia consortium. The recycling capacity of this project is reported to be about 50 000 t/a and the recovered PTA (via methanolysis to DMT and hydrolysis of DMT to PTA) is reused to produce textile polyester in a fiber-to-fiber process (F2F).
2. Technologies available for chemical PET recycling

2.1 Chemical recycling of polyester by glycolysis to produce BHET – 2-(2-hydroxyethyl terephthalate)

- Form the chemistry the glycolysis of polyester to the monomer BEHT is simple. In presence of excess MEG, catalyst, temperature and pressure the PET backbone is destructed. The obtained crude BEHT is refined by filtration, trans-crystallization and/or multi step fine vacuum rectification [patent examples: 5,869,543; 4,078,143 and 5,710,315; literature example: http://www.nt.ntnu.no/users/skoge/prost/proceedings/icheap8-pres07/icheap8webpapers/205%20Moral.pdf]

- Scaling up the total glycolysis to industrial size several hurdles are occurring which are MEG conversion to DEG and acetaldehyde. These side reactions are accelerated by inherent impurities coming from waste stream and are a negative cost factor. Also purification by fine vacuum distillation is extensive and energy intensive.

- One hurdle is that BHET (as raw material to produce polyester) is no commercial product and should be converted advantageously to polyester direct at site of its production.

- Till today only one company in Japan (PET rebirth Co. Ltd) erected a stand alone polyester recycling plant based on total glycolysis. Unfortunately PET rebirth Ltd. went backups and was acquired in 2008 by the company Toyo Seikan Kaisha Ltd. There is to date no information about the status of operation of this glycolysis plant.

2.2 Chemical recycling of polyester by partial glycolysis to produce polyester oligomers

- Broadly applied is the partial glycolysis where the PET-molecule is partially destructed by reacting with MEG to low molecular weight oligomer.

- The glycolysis reaction of PET waste and MEG is mostly carried out by extrusion applying extrusion equipment like single screw, twin screw or multi screw extruder like for instance multi rotation system (MRS).

- The low dynamic viscosity of PET oligomer facilitate a by fare more efficient filtration and removal of impurities. A welcome side effect is the reduced shear stress during extrusion and the lower melting temperature.

- The sketch below (picture 1) demonstrates the design principle of a partial glycolysis unit. Picture 2 is demonstrating a practical example of a partial glycolysis unit.

- Picture 3 is demonstrating examples of chemical recycling by feeding PET pellets/flakes or powder, PET melt or partially glycolized PET to a conventional PET-process.

Picture 1: Design sketch of a partial glycolysis unit
Picture 2: Partial glycolysis unit existing of twin screw extrusion (Coperion) and filtration cascade (Gneuss)

Source: U. Thiele; Polyester Bottle Resins, Production, Processing, Properties and Recycling
PETplanet print Vol 5, 2007

Picture 3: Partial Chemical Recycling by feeding PET pellets/flakes or powder, PET melt or partially glycolized PET to a conventional PET-process

Source: U. Thiele; Polyester Bottle Resins, Production, Processing, Properties and Recycling
PETplanet print Vol 5, 2007
2.3 Chemical recycling of polyester by methanolysis producing DMT

- The chemical recycling applying methanolysis of polyester production waste back to DMT is as old as the polyester production based on DMT.

- In the former time many of the DMT producer have been at the same time polyester producer and so it was very likely to establish a pressure methanolysis vessel where all spinning waste was recycled to crude DMT. This crude DMT was than partially added to the virgin crude DMT and commonly purified and distilled.

- The polyester recycling based on methanolysis using collected polyester waste fractions like bottles / bottle flakes or used textiles is NOT to compare with the in-house recycling of production scrap from spinning because:
  ~ comparable high concentration of impurities
  ~ broad range of organic and inorganic impurities
  ~ kinds of impurities and concentration level fluctuating, no constant input
  ~ additional comonomers like isophthalic acid, cyclohexane dimethanol or di-ethylene glycol are present in the waste

- It is NOT feasible to use unsorted and non-cleaned polyester waste as feed material for chemical recycling.

- Quality requirement to the feed material is high which means the waste must be pre-cleaned similarly like it is usually common during PET flake production.

2.4 Chemical recycling of polyester by hydrolysis producing PTA

- Research work and attempts to produce PTA from polyester waste in pilot plant size have been created in higher numbers. The chemical approaches are versatile like for instance.
  ~ hydrolysis of PET waste in presence of water and acids under pressure and temperature
  ~ hydrolysis / methanolysis under super critical pressure [see also USP 6,262,294]
  ~ stepwise degradation of PET waste by methanolysis and subsequent hydrolysis; [see also USP 5,886,057]
  ~ hydrolysis / acidolysis of PET waste in presence of acid anhydride [see also 6,562,877]
  ~ hydrolysis of PET waste in presence of alkaline, alkaline salt or ammonia [see also: USP 6,720,448; 6,649,792]

- Notwithstanding there are many theoretically worked out approaches known to recycle polyester waste to terephthalic acid. But the only commercialized recycling path which is producing PTA from polyester waste on industrial scale is the destruction of the PET macromolecule by methanolysis to get crude DMT, purification of DMT and subsequently hydrolyzing DMT to PTA.

- One major process hurdle to produce PTA directly from PET scrap are all kinds of impurities which are insoluble in hydrous agents and therefore not removable by trans-crystallization using acetic acid / water. Therefore the loopway via DMT is seemingly useful and necessary.
3. Economy, logistic and process hurdles entering a stand alone polyester chemical recycling project based on

3.1 Economy hurdles
- The economy of scale to produce polyester raw materials like DMT or PTA from polyester waste is the main obstacle to enter in a stand alone project for chemical polyester recycling.
- PTA production plants are today usually > 600 t/d.
- Chemical recycling plant not feasible at capacity < 50,000 t/a (~ 150 t/d).
- As more pre-cleaning is required prior entering chemical recycling plant as higher becomes the risk, that those polyester waste materials like clean bottle flakes are realizing higher margins in the market and are – at a certain price level - not any more useful in the chemical recycling because of financial losses.
- These effects was for instance the driving force of Teijin to change from their bottle to bottle approach, where raw material was bottle flakes to a fiber to fiber or a bottle to fiber approach in their chemical recycling operations in cooperation with Patagonia (see also http://www.teijin.co.jp/english/news/2008/ebd081002.html).
- One thinkable economical reason of Teijin changing from B2B to B2F and F2F process is, that B2B bottle resins are pricewise NOT different or even lower rated than virgin PET resins. But in the opposite polyester textiles based on fiber from 100% recycling are achieving a price premium in several regions of the world (USA, EU) because of their obvious environmentally friendly character (and label).

3.2 Logistic hurdles:
- Feeding a 150 t/d polyester chemical recycling plant exclusively with polyester waste of consistent quality and composition a highly organized system of collectors, sorters, intermediate storages and transporters is required.
- Such kind of plant is based on continuous process technology and needs to run uninterrupted over the distance of minimum one year.
- One possible future way out of this situation is a long-ranging organized and established cooperation between for instance polyester textile producers, textile distributors, consumer and polyester recycler.
- The environmental movement “Cradle To Cradle” or in short C2C could be used as supporting tool to implement such a closed loop between polyester yarn producer, textile apparel, bedding producer or outdoor goods producer, distributors like for instance Walmart or IKEA and the recycled yarn producer. [see also http://www.c2ccertified.com/]
- Prerequisites of such a closed loop C2C process are:
  - the design of the consumer good must be based on 100% recycle ability (for instance 100% polyester)
  - the consumer is getting an incentive to bring the used product after its lifetime back to the distributor or
  - the consumer only leases the products
  - the distributor is becoming at the same time the collector of the used textiles
- Because this concept is the total opposite of our currently all over the world practiced disposable- or throw-away-society it might need a longer time range from now and further increasing shortage of carbon based raw materials until such closed loops of sufficient capacity are organized and installed in larger number.
3.3 Process hurdles

- Comparable to mechanical polyester recycling or reclaiming the chemical recycling needs to have a certain grade of purity of the input waste stream.

- The idea to use the chemical recycling at the same time as separation process for all kind of possible waste like paper, polyolefins, PVC, polyamides, PLA, PS, PAS, wood, metals, sand and so on is not working properly, because it is a prerequisite for a defined recycling process to have a specified and defined feed material.

- Each component of the input waste stream which is different from polyester is causing different side reactions and needs to get its specific treatment coupled to a specific process step to separate it.

- Consequently efficient pre-sorting is required.

- Especially polyester textiles are very often blends of different fiber materials like polyamide, polycrylnitrile, polyurethane, cotton, wool or linen. All such blends are not useful in chemical recycling till now.

- As discussed in the foregoing slides in case of textile polyester recycling the input material should be a polyester mono-fraction.

- Compared to the mechanical polyester recycling the chemical polyester recycling is a complex chemical process which needs all the expertise of production and handling of DMT, PTA and MEG.

4. How to reduce the entrance barrier for investors to enter polyester chemical recycling?

- Stand alone, green field or turn-key projects to enter in polyester chemical recycling will for the time being and possibly also for the next 10 years not appear.

- The most common approach is like observed in Japan (Teijin) the integration of polyester recycling operations into an existent large polyester production site where at the same time polyester raw materials like for instance PTA, DMT and MEG are produced.

- Because methanolysis in combination with glycolysis are processes of relative low temperature levels which is reducing the destruction of contaminants this path is predestined to enter chemical polyester recycling.

- There are existing several polyester producers - also here in China - which are still operating or having mothballed older DMT production lines where especially the whole DMT refinery like trans-crystallization and vacuum distillation equipment, DMT storage and methanol circuit are available.

- For those chemical companies the entrance barrier into chemical polyester recycling, especially in case of possible joint use of existing equipment is lower. Even better such companies are possessing the required chemical know how.

- To assure the feed waste material continuously in amount and composition the long term cooperation with waste collectors is probably the most important step prior of any further investment planning in chemical polyester recycling.
5. Summary

- Three reaction schemes for chemical recycling of polyester – glycolysis, methanolysis and hydrolysis are from know how and basic knowledge available.

- Applied already in the polyester industry is the partial glycolysis where waste material is degraded to oligomers by MEG, fine filtered and directly fed back into existing polyester production lines.

- The most probable path of chemical recycling will combine glycolysis/methanolysis and hydrolysis to produce standard PTA.

- The entrance hurdles for investors to go in large scale chemical polyester recycling are the price difference input mechanical and chemical recycling, the economy of scale (plant size of > 150t/d), the logistic difficulties to provide continuously the feed material and the fact, that chemical recycling needs to have low level impurity input material.

- The Cradle to Cradle movement of the western hemisphere might be a starting point to enter chemical recycling of polyester textiles where one important issue is that desired input waste is mono-fraction textile material.

- Low entrance barrier for chemical polyester recycling are having those polyester producing companies which are still possessing an at site DMT/PTA production which is enabling the joint use of the existing equipment, technology and know how.