

Viscose fibres

A reference book for the Industry

Promotion of Benchmarking Tools for Energy Conservation in Energy Intensive Industries in China

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Disclaimer

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Summary and Acknowledgments

This reference book for the viscose fibre (rayon) industry is a compilation of best available technologies methodologies and future development in this industry. The main information was extracted from the “Reference Document on Best Available Techniques in Polymers Industries (BREF)” published by the Integrated Pollution Prevention and Control (IPPC) Board of the European Commission (2006). Thus the lecture of present reference book should be continued with the cited source.

As part of the BMT-Tool set (BMT = Benchmarking – Monitoring – Targeting) this reference book provides sector specific information regarding the polymer industry in general, frequently used technologies, energy consumption of key processes and other relevant aspects connected with the energy and environment performance of the industry. After the introduction more specific aspects of viscose production are discussed; thereby describing the common processes and the differences of the main production routes: staple fibre and filament yarn.

It has to be noted that this reference book cannot answer all questions related with energy efficiency/intensity in the viscose industry. In fact, this industry could be generally described as energy intensive. But in practice other environmental issues of this industry are more in the spotlight, such as waste water, sulphuric emissions and other chemicals and wastes. Therefore, it is rather difficult to find qualified information on energy consumption related to different fibre grades and product qualities, energy efficient technologies, and energy practices and usage within the viscose industry. Therefore, it is difficult to present energy consumption values associated with the use of BAT. The ranges of energy consumption shown in this reference book should only be taken as an indication about the approximate need of process heat and power at energy efficient factories.

Besides this it is hoped that this reference book will be of some guide towards more energy efficiency in the industry.

1 Introduction - Polymers

The viscose fibre industry belongs to the big group of polymer manufacturing companies.

A polymer (from Greek polis = many and meros = part) is a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds. While polymer in popular usage suggests plastic, the term actually refers to a large class of natural and synthetic materials with a variety of properties.

Due to the extraordinary range of properties accessible in polymeric materials, they have come to play an essential and ubiquitous role in everyday life - from plastics and elastomers on the one hand to natural biopolymers such as DNA and proteins that are essential for life on the other. A simple example is polyethylene, whose repeating unit is based on ethylene monomer. Most commonly, as in this example, the continuously linked backbone of a polymer consists mainly of carbon atoms. However, other structures do exist; for example, elements such as silicon form familiar materials such as silicones, examples being silly putty and waterproof plumbing sealant. The backbone of DNA is in fact based on a phosphodiester bond, and repeating units of polysaccharides (e.g. cellulose) are joined together by glycosidic bonds via oxygen atoms.

Natural polymeric materials such as shellac, amber, and natural rubber have been in use for centuries. Biopolymers such as proteins and nucleic acids play crucial roles in biological processes. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper.

The list of synthetic polymers includes synthetic rubber, Bakelite, neoprene, nylon, PVC, polystyrene, polyacrylonitrile, PVB, silicone, and many more such as viscose fibres.

1.1 Main polymer groups

Polymer companies produce a variety of basic products, which range from commodities to high added-value materials and are produced in both batch and

continuous processes covering installations with a capacity of some 10000 tonnes per year up to some 300000 tonnes per year. The basic polymers are sold to processing companies, serving an immense range of end-user markets. The most commonly used synthetic polymers are as follows:

- Polyolefines (e.g. Polyethylene is the most widely produced polymer worldwide and everyone comes into contact with it daily)
- Polystyrene (a widely used thermoplastic used in packaging, insulation and for many other purposes)
- Polyvinyl chloride (commonly know as PVC)
- Synthetic rubber (e.g. Styrene butadiene rubber, Solution styrene butadiene rubber)
- Polyamides (e.g. Nylon, which was the first ever synthetised polyamid)
- Polyester (of which hundreds of different formulations are brought to the market, e.g. in form of polyester fibres)
- Viscose fibres (made from regenerated cellulose)

1.2 Uses of polymers

The very flexible building principle equips polymers with an extensive range of properties and property combinations. Polymers in the shape of objects, fibres or films may be:

- rigid or flexible
- transparent, translucent or opaque
- hard or soft
- weather resistant or degradable
- resistant to either high or low temperature

In addition, they may be compounded with fillers, blended with other products (e.g. glass fibres) forming so-called composites or with other polymers yielding polymer blends.

A certain polymer is usually not the only material which can be used in any given field of application. Alternative materials exist and polymers have to be successful in a competitive market. Polymers often bring advantages to numerous applications, for example:

- weight reductions and consequent transport and fuel savings
- electrical insulating properties suitable for wiring, switches, plugs, power tools and electronics
- optical transparency suitable for packaging, lighting and lens applications
- corrosion resistance which is important for plumbing, irrigation, rainwear and sports articles
- resistance to chemicals, fungi and mildew
- ease of processing making complicated shapes possible
- cost savings over alternative solutions

1.3 General processes and techniques applied in the polymer industry

The chemistry of polymer production consists of three basic reaction types, polymerisation, polycondensation and polyaddition, thus the number of operations/processes used remains reasonably small. These include preparation, the reaction itself and the separation of products. In many cases cooling, heating, or the application of vacuum or pressure is necessary. The unavoidable waste streams are treated in recovery and/or abatement systems or disposed of as waste.

The production of polymers follows the scheme given in the figure below with monomers, comonomers, catalysts, solvents as well as energy and water on the input side and the product, off-gases, waste water and wastes on the output side.

The key environmental issues of the polymer sector are emissions of volatile organic compounds, in some cases waste waters with the potential for high loads of organic compounds, relatively large quantities of spent solvents and non-recyclable waste as well as the energy demand. Given the diversity of the sector and the wide range of

polymers produced, this document provides only a small portion of this sector, concentrating on viscose fibre manufacturing only. A complete overview of the releases from the polymer sector can be found in further literature.

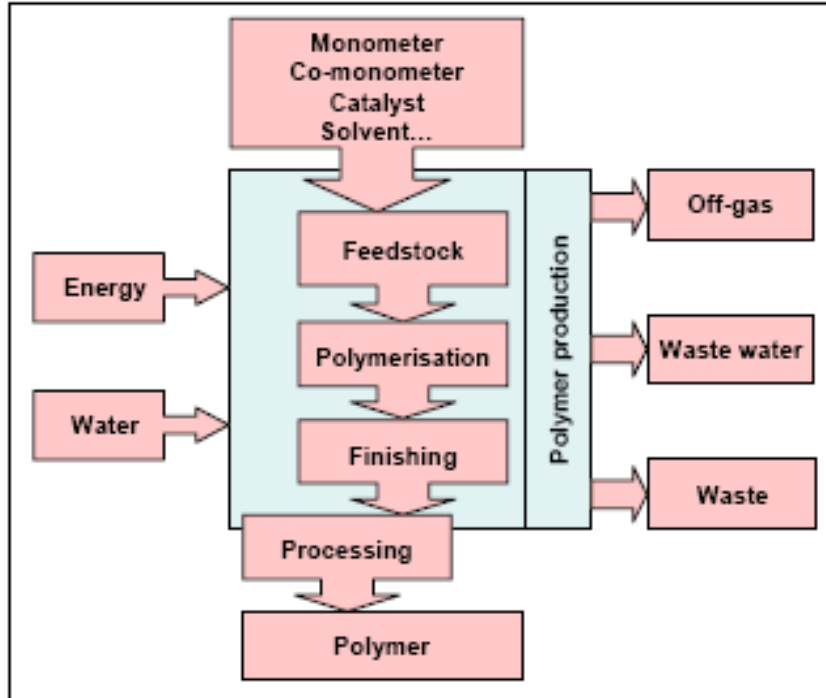


Figure 1.1: General production scheme of polymers

2 Viscose fibres

2.1 Viscose

Viscose is a viscous organic liquid used to make rayon and cellophane. Viscose is becoming synonymous with rayon, a soft material commonly used in shirt, coats, jackets, and other outer wear.

Viscose fibres are made from regenerated cellulose. The process of dissolving pulp (the very viscose solution of pulp gave the name to the fibre product) was an achievement of the industrial revolution of the 19th century. And this innovation triggered the discovery of full synthetic fibres during the 20th century.

Many other cellulose dissolving and regeneration processes like cuprammonium rayon, which was the first process made available for manmade fibres and was already developed in the 1850s, or cellulose derivatives (like acetate) were in competition with the viscose process, but viscose proved to be superior based on process and product performance. Its booming period ended after World War 2 with the introduction of the synthetic competitive products. In the last decade, the production has stabilised at approximately 2.7 million tonnes worldwide (Europe 600000 tonnes).

It is preferably supplied to market end-uses (textile products and nonwovens) where the hydrophilic (moisture absorbing) properties of the material, for instance in direct contact with the skin or with mucous membranes, are relevant.

Currently (2005), about 85 % of the total viscose fibre production is produced as staple fibres and about 15 % as filaments.

It has to be mentioned that a substantial amount of regenerated cellulose in the form of films (cellophane) based on the viscose process are still applied in sausage encasings and other packaging foils.

In recent history in Europe, textile viscose filament end-uses are receiving increased competition (resulting in phasing out of capacity) by cheaper competitive yarns based on polyester and polyamide, whereas viscose staple fibre and viscose tyre cord keep a strong position.

Viscose currently is becoming less common also because of the polluting effects of

carbon disulfide and other by-products of the process, forcing some factories to close.

2.2 Viscose production in China

In 2006, China's total output of viscose staple fiber reached 1.02 million tons and, the production capacity and the output of cotton pulp amounted to 920,000 tons and 886,000 tons respectively.

Altogether there were 27 main companies producing viscose staple fiber by the end of 2006. Among these 27 companies, nine had a production capacity of 50,000 tons or above, and 11 had a production capacity of 20,000 tons or above.

Boosted by the rapid increasing demand of textile, the production capacity of viscose staple fiber is also rapidly expanding. From 2003 to 2006, China's domestic accumulated capacity reached 532,000 tons with a high annual average growth of 22%. The newly-added capacity in 2006 amounted to 180,000 tons. Main companies included Manas Aoyang Science Co., Ltd, Hubei Jingwei Chemical Fiber, Tangshan Sanyou Group, Nanjing Chemical Fibre Co., Ltd, and Xiaoshan Fulida, etc.

Production capacity tends to gather into large companies in recent years. China has three companies with an annual production of 100,000 tons (or above) staple fiber. The production capacity of the three totally reaches 330,000 tons, taking up one half of the total capacity. China has five companies with an annual production of 50,000 (or above) tons staple fiber. The production capacity of the five totally reaches 690,000 tons, which is equal to 59.5% of the total capacity. At the same time, along with the construction and the practice of large-capacity production lines, the small-size staple fiber production lines will be gradually eliminated. It is estimated that altogether 134,600 tons of production capacity will be eliminated from 2003 to 2006.

It is forecasted that production of viscose staple fiber in China will reach 1.80 million tons in 2010 and the market demand will be 1.78 million tons. In addition, the differentiation rate of viscose staple fiber in 2010 will reach or surpass 50%. At that time, the amount of viscose staple fiber with different varieties and different functions will exceed 800,000 tons.

Demand for viscose staple fiber from 2007 to 2009 is estimated to grow at 14% and

the production is estimated to grow at 15% yearly. Imports will maintain the current level or decline slightly. The exports will increase at an annual rate of about 15%.

2.3 Processes (staple fibres and filament yarn)

When producing viscose fibres, the pulp – which is mainly cellulose from wood – is dissolved and subsequently precipitated under controlled conditions. The most important process worldwide is the so-called ‘viscose process’ where the alkaline pulp is treated with carbon disulphide (CS₂) and dissolved by adding sodium hydroxide solution. A viscous orange-brown solution called ‘viscose’ is formed which is ripened, degassed and then pressed through spinnerets into a highly acidic spinning bath. Here, the cellulose precipitates when CS₂ and the by-product H₂S is released. After this, the cellulose is stretched, washed and then undergoes further processing.

At this point, a distinction has to be made between staple fibres and filament yarn:

- Staple fibres are cut into short pieces after the spinning bath. These short fibres, which are each approximately 4 cm long, are spun into textile yarns or processed into ‘non-woven’ products later on.
- In contrast, filament yarns are spun into endless fibres which can be used immediately.

Viscose products for textile usage with certain improved product characteristics are called ‘modal fibres’.

Regular rayon (or viscose) is the most widely produced form of rayon. This method of rayon production has been utilized since the early 1900s and it has the ability to produce either filament or staple fibers. The process is as follows:

Cellulose: Production begins with processed cellulose

Immersion: The cellulose is dissolved in caustic soda: $(C_6H_{10}O_5)_n + nNaOH \rightarrow (C_6H_9O_4ONa)_n + nH_2O$

Pressing: The solution is then pressed between rollers to remove excess liquid

White Crumb: The pressed sheets are crumbled or shredded to produce what is known as "white crumb"

Aging: The "white crumb" aged through exposure to oxygen

Xanthation: The aged "white crumb" is mixed with carbon disulfide in a process known as **Xanthation**, the aged alkali cellulose crumbs are placed in vats and are allowed to react with carbon disulfide under controlled temperature (20 to 30°C) to form cellulose xanthate: $(C_6H_9O_4ONa)_n + nCS_2 \rightarrow (C_6H_9O_4O-SC-SNa)_n$

Yellow Crumb: Xanthation changes the chemical makeup of the cellulose mixture and the resulting product is now called "yellow crumb"

Viscose: The "yellow crumb" is dissolved in a caustic solution to form viscose

Ripening: The viscose is set to stand for a period of time, allowing it to ripen: $(C_6H_9O_4O-SC-SNa)_n + nH_2O \rightarrow (C_6H_{10}O_5)_n + nCS_2 + nNaOH$

Filtering: After ripening, the viscose is filtered to remove any undissolved particles

Degassing: Any bubbles of air are pressed from the viscose in a degassing process

Extruding: The viscose solution is extruded through a spinneret, which resembles a shower head with many small holes

Acid Bath: As the viscose exits the spinneret, it lands in a bath of sulfuric acid, resulting in the formation of rayon filaments: $(C_6H_9O_4O-SC-SNa)_n + \frac{1}{2}nH_2SO_4 \rightarrow (C_6H_{10}O_5)_n + nCS_2 + \frac{1}{2}nNa_2SO_4$

Drawing: The rayon filaments are stretched, known as drawing, to straighten out the fibers

Washing: The fibers are then washed to remove any residual chemicals

The basic process ends here. Depending on the desired product it is continued optional by

Cutting: The filaments are cut down when producing staple fibers

Spinning: Filament yarns are spun into endless fibres

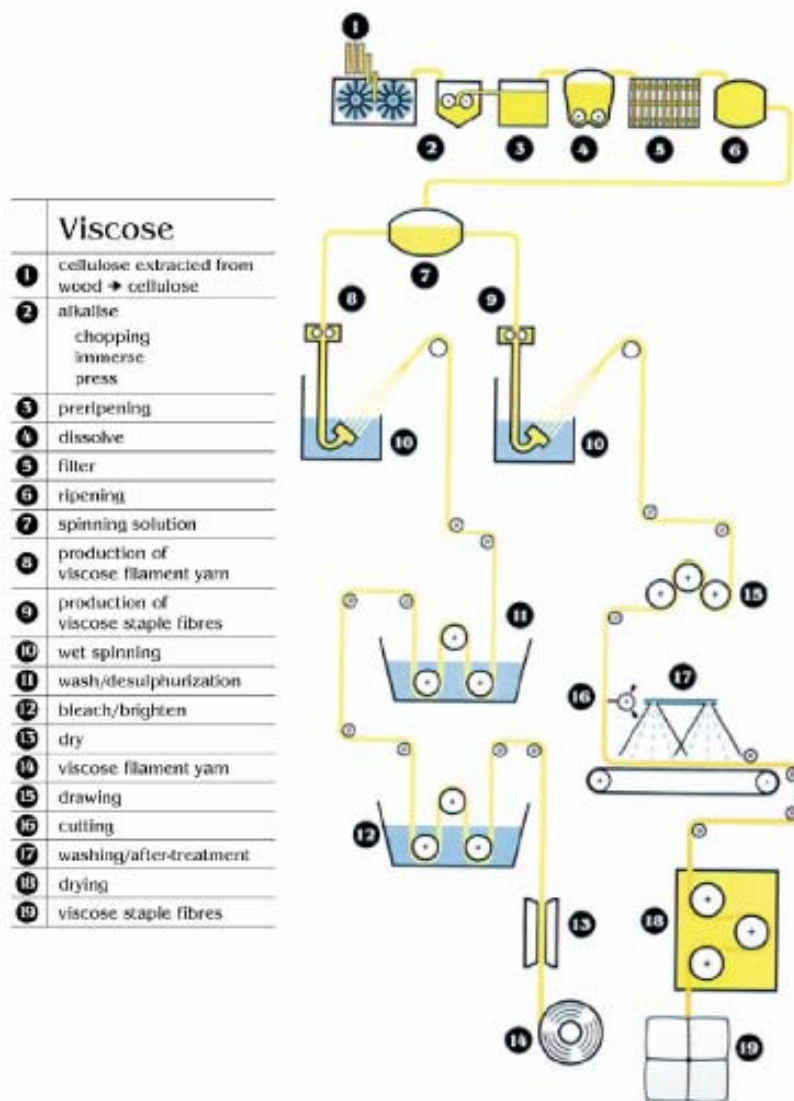


Figure 2.2 gives a schematic view of both staple fibre and filament yarn production.

2.4 Production of filament yarns

Until the spinning step, the process is very similar to the production of staple fibres (see Figure 2.2).

Long fibred pulp is used as the raw material. For the first step, it is treated with diluted sodium hydroxide solution (approximately 15 %). Afterwards, the liquid is removed by pressing and then it is recycled back into the process together with fresh NaOH. Next, the pulp sheets are defibrated, pre-ripened and put into CS₂ for chemical conversion to xanthate. After the addition of aqueous NaOH, the viscose emerges which is ripened and degassed in vacuum prior to spinning.

Depending on the quality of the fibres, the spinnerets have different numbers of holes ranging from 30 to more than 2000. The spinning bath is sulphur acidic and contains high concentrations of sodium sulphate (Na₂SO₄) and zinc sulphate (ZnSO₄).

Three different spinning methods are used:

- pot spinning – the viscose is pressed directly into the spinning bath. This is possible for threads from the size of 67 to 1330 dtex^{*}
- continuous spinning – the viscose is pressed through the spinneret into a spinning tube where the flowing spinning bath picks up the coagulating fibre. This is again possible for threads from the size of 67 to 1330 dtex
- bobbin spinning – this process is similar to continuous spinning, but the fibre is fully coagulated. In order to achieve this, it is let into a second spinning bath where the coagulation is finished. This technique is possible for threads from the size of 1220 to 2440 dtex.

After spinning, the fibres are washed, finished, dried and spooled.

Currently, there are installations with integrated as well as batch washing.

^{*} 1 dtex = 1 g/10000 m of fibre

2.5 Lyocell fibres

Since 1998 the Lyocell process has been used in Austria and the special feature of this process is the solution of the pulp which is in an organic solvent (NMMO = N-methylmorpholine-N-oxide), instead of CS₂/NaOH, which has the effect of eliminating the odorous and noxious emission of sulphurous gases. The properties of the products from this Lyocell process are different to the standard viscose fibre, and therefore this process should not be regarded as an environmentally compatible alternative to the viscose process.

The core part of the Lyocell process is the direct dissolution of cellulose through NMMO (N-methyl-morpholine-n-oxide). The solvent, which is 100 % biodegradable, is able to dissolve cellulose physically without any chemical pretreatment.

Therefore, the chopped pulp is mixed with NMMO. Water is removed from the so-called 'premix' to form a solution, which is then filtrated and spun through spinnerets into an aqueous NMMO solution to make the filaments.

The wet filaments are cut and the staples run through several after-treatment sections. After washing out residual NMMO, spin finish is applied and the fibre is dried and packed.

Through a multistage cleaning process, more than 99.6 % of the solvent can be recovered. Also the water that is regained during the evaporation step is recycled back into the washing section of the fibre line.

This leads to a low specific water demand and overall low environmental emission figures.

Generally, the process includes the following steps:

- dissolving
- spinning
- precipitating
- washing
- finishing
- drying

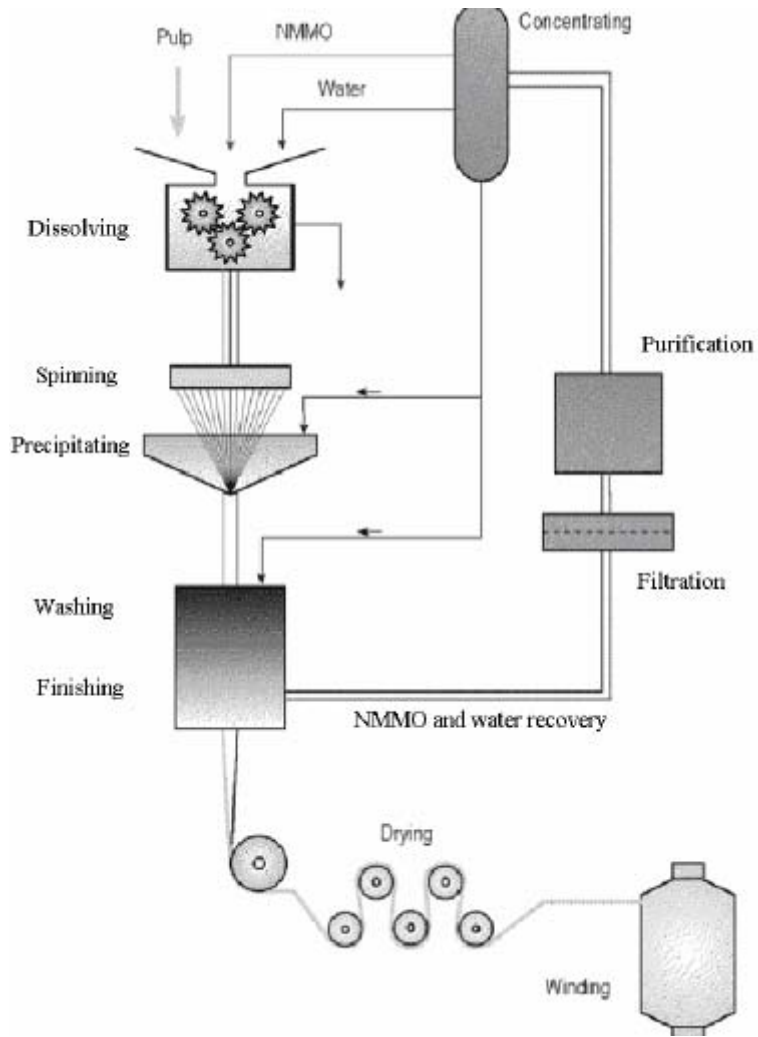


Figure 2.4 shows a simplified diagram of the Lyocell process.

3 Consumption and emissions

3.1 Water and waste water and other emissions

The viscose process results in considerable waste waters, both in respect to volume and discharges. The main sources are:

- spent caustic from the pulp alkalisation and pressure filtration
- maintenance of the filtration units
- spent acid spinning bath solution
- purges from neutral or (sub) alkaline baths/conditioning steps
- vacuum units (steam-jet pumps with contact condensers, water seal pumps)
- waste gas scrubbing

The total waste water volume depends mainly on the vacuum generation (steam-jet pumps consume far more water than water seal pumps with closed seal water loops) and on the spinning and conditioning steps. The options for re-use and treatment of the various waste water streams depend on the given composition.

Table 3.1a summarises data for staple fibres, Table 3.1b for filament yarns.

| Staple fibres | Unit | [37, CIRFS, 2004] | [30, UBA, 2004] | Comment |
|--|-------------|--------------------------|------------------------|--|
| Consumptions per tonne of product | | | | |
| Process water | t | 35 - 130 | | Low values referring to closed systems, depending on local aquatic conditions |
| Cooling water | t | 189 -260 | | Depends on condensation technology for spinning bath and local aquatic conditions |
| Pulp | t | 1.035 -1.065 | | Depends on pulp specification, values based on conditioned pulp |
| CS ₂ | kg | 80 -100 | 91 | Depends on recovery technology and washing technology |
| H ₂ SO ₄ | t | 0.6 -1.03 | | High values correspond with lower energy consumption at spin bath and second bath recovery, depends also on fibre specifications |
| NaOH | t | 0.5 -0.7 | 0.56 | Including waste gas/water treatment |
| Zn | kg | 2 -10 | 20 | Depending on fibre specifications and end uses |

| | | | | |
|---------------------------------------|-----|-----------|-----------------------|---|
| Spin finish | kg | 3 -5.3 | | Depending on fibre specifications and end uses |
| NaOCl | kg | 0 -50 | | Depending on fibre specifications and end uses, resp. the use of alternative bleaching agents |
| Emissions per tonne of product | | | | |
| S to air | kg | 12.5 -30 | 17.04 CS2 0.21 H2S | Depends on CS2 consumption |
| SO4 2- to water | kg | 230 -495 | | Depends on sulphuric acid consumption and fibre properties |
| Zn to water | g | 30 -160 | 15 - 40 | Depends on Zn consumption and spin bath recovery technology |
| AOX | g | 10 -20 | | |
| COD | kg | 3.8 -8 | 3.3 | |
| Hazardous waste | kg | 0.2 - 2.0 | 3 | From utilities and maintenance operations |
| Noise at the fence | dBA | 55 -70 | | Depends on the local situation |

| Filament yarn | Unit | Filament production with integrated washing | Filament production with batch washing | Comment |
|--|-------------|--|---|---|
| Consumptions per tonne of product | | | | |
| Water | t | 152 - 500 | 120 - 140 | Including cooling and process water |
| Pulp | t | 1.0 - 1.1 | 1 - 1.2 | Depends on pulp specification |
| CS2 | kg | 290 - 300 | 90 - 100 | Depends on recovery technology and washing technology |
| H2SO4 | t | 0.9 - 1.6 | 0.9 - 1 | |
| NaOH | t | 0.7 - 1.0 | 0.7 - 1 | Including waste gas/water treatment |
| Zn | kg | 10 - 18 | 8 - 13 | Depends on fibre specifications and end uses |
| Spin finish | kg | 3 - 24 | 8 - 18 | Depends on fibre specifications and end uses |
| NaOCl | kg | 0 - 0.2 | 0 | Depends on end uses and the use of alternative bleaching agents |
| Emissions per tonne of product | | | | |
| S to air | kg | 170 - 210 | 40 - 60 | |
| Waste water | t | 35 - 130 | 60 | |
| SO4 2- to water | kg | 250 - 1000 | 200 - 350 | Depends on sulphuric acid consumption and fibre properties |

| | | | | |
|--------------------|-----|------------|-----------|--|
| Zn to water | g | 500 - 3000 | 100 - 300 | Depends on spin bath recovery technology and waste water treatment |
| AOX | g | 7 - 50 | 5 | |
| COD | kg | 6 - 28 | 5 - 6 | |
| Hazardous waste | kg | 0.2 - 5 | 1 - 5 | From utilities and maintenance operations |
| Noise at the fence | dBA | 45 - 70 | | Depends on the local situation |

3.2 Energy use and energy benchmarks

The demand for energy depends on the local situation if the polymerisation unit is integrated into a larger complex with, for example, the need for low pressure steam or not. Thus, the swap of energy between different plant sites has to be taken into account.

Thus energy benchmarks can only be expressed as ranges from-to, whereas the following numbers are reported:

- Energy intensity for staple fibres
26.1 – 33.2 GJ per ton of product
- Energy intensity for filament yarn
83 - 125 GJ per ton of product (Filament production with integrated washing)
70 - 82 GJ per ton of product (Filament production with batch washing)

4 Best Available Technologies

It is referred to the main source of this reference book, which is the BAT document on Best Available Technologies in the Polymer Industry, published by the EU in 2006 (see references and links).

This document lists a big number of general BATs for the polymer industry in total and additional specific measures recommended for viscose fibre production. Most of the recommendations are not explicitly linked with energy, many with waste water, emissions and general practices like EMS, good housekeeping, etc. Apparently these options will influence also the energy consumption of an operation, by increasing the overall efficiency of the operation. As an example the proper housing of the spinning frames and departments will lead to higher energy efficiency, lower emissions and recovery of agents like sulphuric agents.

Like other industries external benchmarking is only one further step after setting up adequate internal benchmarking systems with monitoring and targeting as a permanent task.

5 References and Links

BEST AVAILABLE TECHNIQUES IN THE PRODUCTION OF POLYMERS,
CEMBUREAU 2006 - <http://www.epa.ie/downloads/advice/brefs/Polymers.pdf>

http://www.lenzing.com/images/lenzing_kk/NH_Brosch_EN_2008_SCREEN.pdf

<http://www.lenzing.com/nonwovens/de/nonwovensfibers/3197.jsp>

More information can be found by searching in the internet.