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EXERGETIC ANALYSIS OF THE THERMAL CONVERSION PROCESS IN PAN-BASED CARBON FIBRE PRODUCTION

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ABSTRACT: The processes of stabilisation and carbonisation in carbon fibre manufacture provides a large energy saving potential if an adequate furnace technology and process control is used. In this paper a general exergetic balance equation for the processes of stabilisation and carbonisation with the objective to determine the exergetic costs of producing carbon fibres is placed. After a short theoretical explanation of the carbon fibre manufacturing processes, this paper will resort to the general laws of thermodynamics and later determine the exergy of heat and mass flows in the processes. Experiments are carried out in a DSC and TGA combined with a mass spectrometry to determine the composition of the evolved gases during the stabilisation process. Furthermore DSC and TGA measurements are used to determine specific heat capacity and mass loss of the polyacrylonitrile precursor material. Included in the exergetic balance equation the measured material values leads to an exergy efficiency result of the carbon fibre conversion reaction.

Keywords: carbon fibre; exergy; stabilisation; energy efficiency

PAN ESASLI KARBON LİF ÜRETİMİNDE TERMAL DÖNÜŞÜM PROSESİNİN EKZERJETİK ANALİZİ

ÖZET: Karbon lif üretimindeki stabilizasyon ve karbonizasyon prosesi, yeterli bir ısıtma teknolojisi ve kontrol prosesi kullanıldığı takdirde büyük bir enerji tasarruf potansiyeli sağlamaktadır. Bu çalışmada, karbon lif üretiminin ekzerjetik maliyetlerinin belirlenmesi amacıyla stabilizasyon ve karbonizasyon prosesleri için genel bir ekzerjetik denge eşitliği konu edilmiştir. Karbon lif üretim prosesine yönelik kısa bir teorik açıklamanın ardından termodinamiğin temel kanunlarına değinilmiş ve daha sonra sözkonusu proseslerdeki ısı ve kütle ekzerjisi tanımlanmıştır. Stabilizasyon prosesi süresince ortaya çıkan gazların içeriğinin belirlenmesi amacıyla kütle spektrometresi ile kombine edilmiş DSC ve TGA ölçümleri yapılmıştır. Ayrıca, öncül poliakrilonitril malzemesinin kütle kaybı ve spesifik ısı kapasitesinin belirlenmesi amacıyla da DSC ve TGA ölçümleri gerçekleştirilmiştir. Ekzerjetik denge eşitliğine ilave edilmiş ölçülen malzeme değerleri karbon lif dönüşüm reaksiyonunun ekzerji verimlilik sonuçlarına ulaşılmasını sağlamıştır.

Anahtar Kelimeler: karbon lif; ekserji; stabilizasyon; enerji verimliliği

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1. INTRODUCTION

Energy as a valuable source which needs to be used economically gets recently more and more into the point of interest in the field of carbon fibre manufacturing as an energy intensive process. One of the main ambitions in the area of energy engineering is to analyse the process of polymerization and thermal decomposition of a polyacrylonitrile-precursor (PAN) in order to improve the efficiency.

The resulting energy savings will decrease the production costs of the carbon fibre and therefore establish an advantageous position on the market. This financial improvement results in an increased attraction in many fields, e.g. automotive and regenerative energy sector, which helps to create a more general accessibility in those fields.

Carbon fibres offer excellent characteristics and provide a great potential as substitution material for conventional materials in the area of aerospace, automotive, etc. to achieve weight improvements and increase the energy efficiency of those systems. Despite these beneficial mechanical properties, the production of carbon fibres is an energy consuming and cost-intensive process. This leads to a very limited and exclusive range of application. Manufacturing the PAN-Precursor, stabilisation and carbonisation are one of the most expensive processes. In this paper a method for evaluating the exergetic characteristics of the two sub processes stabilisation and carbonisation, which combined represent 37 % of the manufacturing costs, is presented [1]. By the help of different thermal analyses, e.g. the thermal gravimetric analysis (TGA), the differential scanning calorimetry (DSC) and the temperature moduled dynamic differential calorimetry which will be linked to a mass spectrometer (MS) the process specific exergetic flows will be determined and exergetically evaluated. After experimentally and theoretically determining all the necessary exergetic flows, the process efficiency of the thermal decomposition will be calculated with exergetic formulas. The main ambition of this paper is to identify possible potential in energy savings in the thermal decomposition of PAN to carbon fibre. Furthermore increases in energy efficiency are highlighted.

2 EXPERIMENTAL PROCEDURES

2.1 Exergetic evaluation of the thermal conversion

The exergetic evaluation of the process of the thermal conversion is carried out under the circumstance of a transit-adjusted system boundary (Figure 1). Two forms of input exergy can be distinguished: the transit exergy E_T and the feed exergy E_F. In most processes not the whole flow of exergy is responsible for the conversion but just a specific part. This can be e.g. just the thermo-mechanical part of the exergy if an observed material flow changes its temperature and pressure while passing the system boundaries. The chemical part of the exergy is completely obtained and represents therefore the transit part. The transit exergy E_T stays the same while passing the system boundaries, so it can theoretically be laid around it. Thus the exergetic examination is transit free. The part of the exergy which is mainly responsible for the conversion is called feed exergy E_F. Using a standard method like the input-output-examination results only in the possibility to identify the dissipation of the process and the inner loss of exergy. Information about the usability of the leaving flows of exergy or the convertibility of the accessing flow of exergy stay unconsidered. [2]

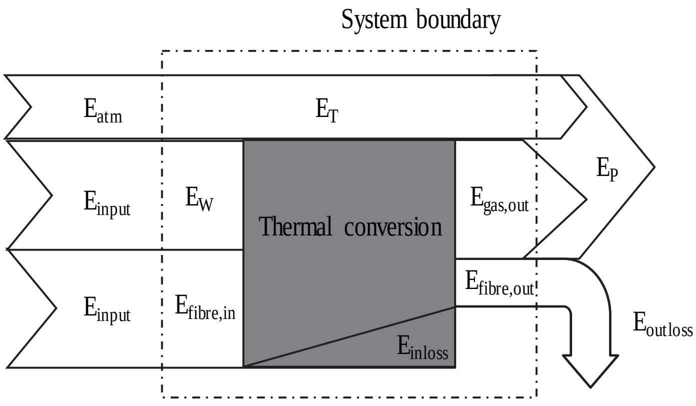

Figure 1. Transit-adjusted system boundary of the thermal conversion process

In Figure 1 the exergy of the applied flow of heat E_W and the exergy of the accessing fibre $E_{fibre,in}$ provide the feed exergy E_F. The flow of exergy of the incoming atmosphere gas E_{atm} will be defined as transit exergy E_T due to the very low participation according to the process reactions. The involvement of air in the stabilisation process will be disregarded.

The exergy of the leaving fibre $E_{fibre,out}$ will be the outer loss of exergy $E_{outloss}$. This exergy cannot be used anymore and will therefore not be included in the exergetic examination. Furthermore the transit exergy E_T and the exergy of the evolved gases $E_{gas,out}$ define the usable form of exergy of the system boundary called the product exergy E_P. Assuming that the whole flow of gas after the stabilisation and carbonisation is exergetically used, the following exergetic equation can be developed:

$$E_{fibre,in} + E_W = E_{fibre,out} + E_{gas,out} + E_{inloss} \tag{1}$$

where E_{inloss} is the inner exergy loss of the reaction process due to entropy production in the stabilisation and carbonisation.

Hereby the equations for calculating the exergetic heat and mass flows include specific material values and state variables, such as specific heat capacity, which mostly can be found in the relevant literature or determined from the corresponding basic thermodynamic equations. However, a few exceptions are part of the problem. These include the composition of the evolved gas over the process time, which depends on the fibre material, the used atmosphere and the driven temperature profile. The evolved gas composition is experimentally determined with the methods described below. The composition of the evolved gas is determined by means of a thermal gravimetric differential scanning calorimetry combined with a mass spectrometry (TGA-DSC/MS) experiment. After all, the exergy flows have been determined experimentally and theoretically by use of thermal analysis and thermodynamic fundamentals.

2.2 Thermal gravimetric analysis

In order to determine mass changes of a sampling which undergoes a specific temperature profile as a function of temperature or rather time the TG/DSC1 of Mettler Toledo is used for the stabilisation as well as for the carbonisation process. Furthermore the TG/DSC1 is used to determine the mass of evolved gas during the thermal conversion process.

2.3 TG-DSC/mass spectrometry

The out coming result of the mass spectrometry will deliver a spectrum of which the qualitative composition of the evolved gases can be determined. For the experimental investigations a Setsys evolution TG-DSC of the Setaram Instrumentation GmbH (Caluire, France) combined with an Omnistar mass spectrometer of the Pfeiffer Vacuum GmbH (Annecy Cedex, France) is used. The outlet of the TGA/DSC is bonded with a heated capillary tube to the mass spectrometer (MS). The TGA-DSC/MS experiment was realized in the laboratories of the Setaram Instrumentation GmbH (Caluire, France) in air and nitrogen atmosphere.

3 RESULTS

3.1 Thermal experiments

All experiments in the described methods above are carried out with the same temperature profile for stabilisation and carbonisation. Here for a temperature profile with four isothermal segments for the stabilisation under ambivalent air atmosphere and a linear heating temperature profile for the carbonisation under nitrogen atmosphere were used. The stabilisation temperature profile begins at 25°C and heats with a heating rate of 10 °C/min up to 220°C, 240°C, 260°C, 280°C. The first temperature is hold for 40 min and the following three temperatures for 25 min each. After the last isothermal stage the Process is heated up to 300°C with 10 C/min. The carbonisation temperature profile starts at 300 C and heats with a heating rate of 50 C/min up to 1,500 C. The used temperature profile corresponds to the regular temperature profile, which is used for carbon fibre production of PAN based fibres [1].

In the TG-DSC/MS experiments the MS signal of CO (m/z 28) cannot be determined due to the nitrogen in the used atmosphere, since nitrogen has the same atomic mass unit as CO. In the figures 2 and 3 the graph of the heat flow and mass loss for the stabilisation process from the DSC and TG measurement are compared. The first mass loss is represented by an endothermic peak in the heat flow course and the following four are connected to exothermic peaks. The first endothermic peak is due to the evaporation of water out of the fibre material. This is also evident from the logarithmic representation of the H_2O MS signals in figure 4. The four exothermic reaction during the four isotherms are accompanied by the release of CO_2 (m/z 44) , H_2O (m/z 18) and acrylonitrile (m/z 53) (figure 4). The emission of CO_2 results from the oxidation of PAN fibre material and the formation of -COOH groups [1]. The releases of acrylonitrile monomers and H_2O are products of the sub-processes of cyclization and dehydrogenation in the stabilisation process [3]. The emission of acrylonitrile monomers is an indication that the reactions of cyclization and dehydrogenation, as well as the oxidation of PAN are not ideal reactions. Because of erroneous linkages in the polymer itself, the monomers are split off by thermal treatment, so that the detached acrylonitrile monomers are evolved. This splitting off is called homolytic thermal cleavage. Further studies have shown that in addition to the monomer and dimers, trimers, tetramers, pentamers, etc. are released to a limited extent [4], [5].

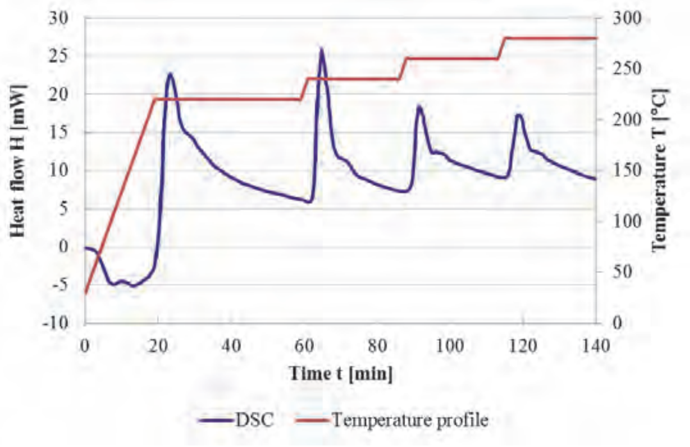

Figure 2 Stabilisation enthalpy course and temperature profile

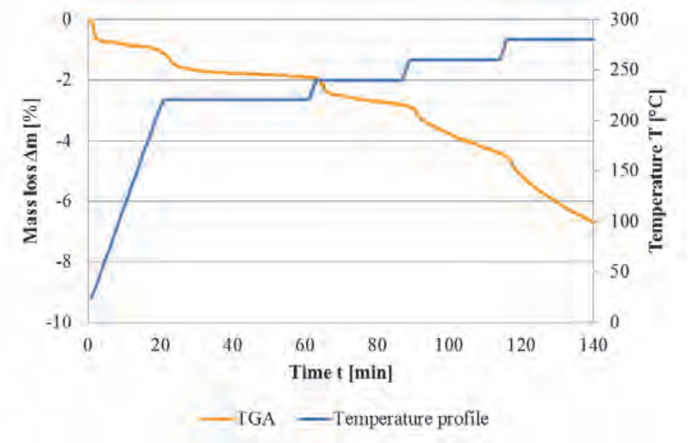

Figure 3 Stabilisation mass loss and temperature profile

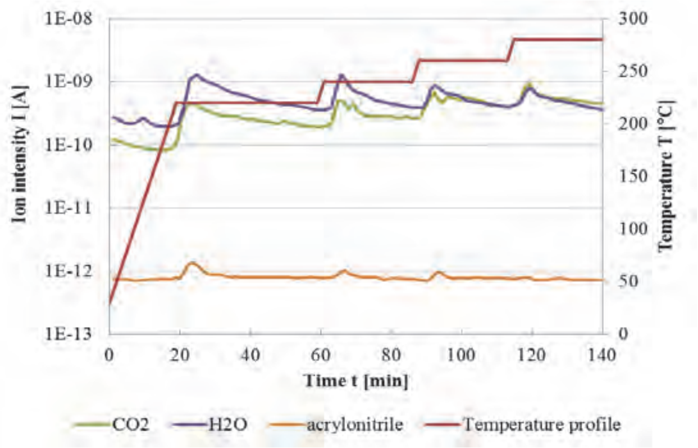

Figure 4. Released gas courses during stabilisation and temperature profile

If the temporal profile of the heat flow is compared with the time course of the MS signals, it can be seen that longer heating times result in higher gas emissions. Where by the rate of gas emission in the isothermal stages decreases slowly. This decline is a sign that the reaction comes to an end and the potential of the isotherms is almost depleted.

In Figure 5 and 6 the overlap of the DSC and TGA courses with the temperature profile during the process of carbonisation in an inert nitrogen atmosphere up to 1,500 °C is shown. In this case, it is observed that the total mass loss of -45.18 % takes place at different times in the process. Further the different mass losses are defined by one exothermic and one endothermic reaction. In table 1, the enthalpy, the onset, offset and peak temperatures of the two major reactions are listed.

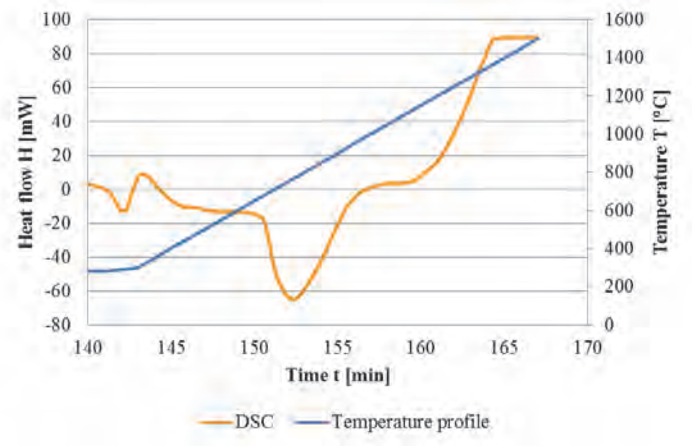

Figure 5. Carbonisation enthalpy course and temperature profile

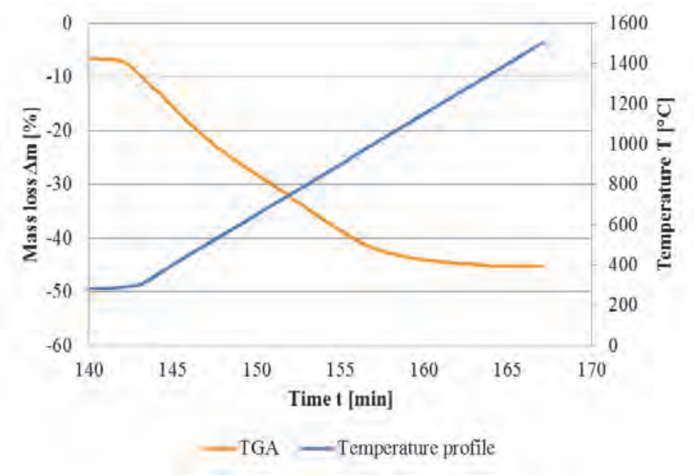

Figure 6. Carbonisation mass loss and temperature profile

Table 1. Enthalpy carbonisation data

Enthalpy h [J/g]	Onset temperature T_{on} [°C]	Offset temperature T_{off} [°C]	Peak temperature T_{peak} [°C]
-95.7	386.2	680	434.2
203.3	802.1	1091	891.1

In Figure 7, the releases of CH_4, NH_3 and H_2O during carbonisation are products of the first exothermic reaction. Here the H_2O emission results from the still ongoing dehydrogenation and cross-linking of the resulting ladder polymer chains via the oxygen groups [1]. CH_4 and NH_3 result by active chain ends or by the end-to-end connection of two ladder polymer chains [3]. Figure 7 also clearly shows the typical two maxima can be identified in the course of release of CH_4 and NH_3 at 450°C and 700°C. The release of H_2 (m/z 2) starts by networking the ladder polymer chains by dehydrogenation at 500°C [1]. The emission of H_2 reaches its maximum at 800°C and decreases with the beginning of the endothermic reaction during the carbonisation. Releases of HCN and N_2 result from the intermolecular polymer chain bonding. In the range of 450°C, the HCN emission is mainly due to the binding of ladder polymer ends. Above 600°C the lateral cross-linking of polymer chains to basal levels takes place. This behaviour is reflected in the two peaks of the HCN profile at 450°C and 800°C. CO_2 emission is further due to the binding of -COOH groups. The emission of hydrocarbon fragments is characterized by a relatively constant course. The release of these arises as a result from the homolytic thermal cleavage of individual hydrogen atoms during the polymer chain crosslinking. The course of acrylonitrile release is similarly determined for HCN release by two peaks at 450°C and 800 C. The elimination of individual acrylonitrile molecules is thus due to the crosslinking of the ladder polymer ends at 450°C and the lateral crosslinking of the polymer chains at 800°C [3]. In figure 7 the curves for carbon fragments C (m/z 12), the atomic mass unit 32 i.a. oxygen O_2 (m/z 32), ethane dinitrile CH=CH-CN (m/z 52) and 2-cyanpropylene CH=C-CH-CN (m/z 64) are represented. The emission process and formation mechanism of carbon fragments is comparable to that of hydrogen fragments. In the course of atomic mass unit 32 a clear first peak can be seen at 450°C and a second at 1200°C. Between the peaks the course drops very sharply and falls under the initial ion intensity. This drop is defined by the oxidation of the PAN fibre material, and the uptake of oxygen from the environment. The first peak coincides with the exothermic reaction of the heat flow course and is due to the release of smaller hydrocarbons and/or nitriles. Analogously to the first

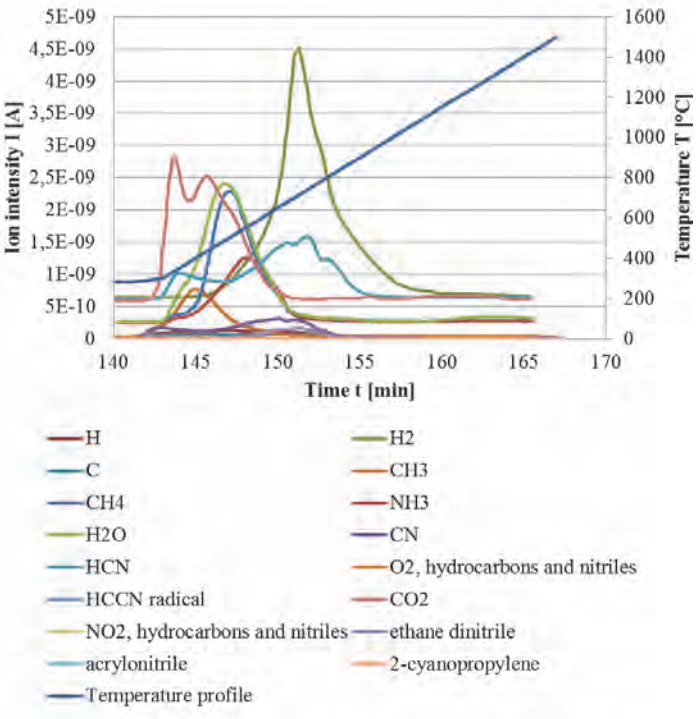

Figure 7. Released gas courses during carbonisation and temperature profile

peak the second one at 1200°C is determined by the further release of small hydrocarbons and nitriles. The release of ethane dinitrile has analogous to the HCNemission peaks at 450°C and 800°C. Ethane dinitrile generated by homolytic thermal cleavage of Propylidene-malononitrile molecules, which are decomposed in ethane dinitrile and 2-cyanpropylene. The mechanism for ethane dinitrile and 2-cyanpropylene is schematically shown in Figure 8. [4], [5].

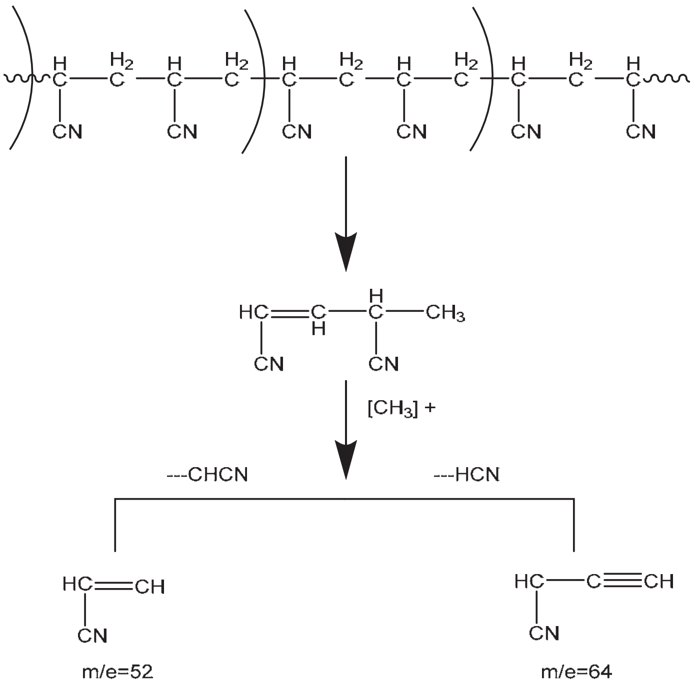

Figure 8. Mechanism for the ethane dinitrile and 2-cyanopropylene releases [5]

3.2 Exergetic assessment of the thermal conversion

For the further consideration of the exergetic thermal conversion the specific values of all in the process involved exergy flows are listed in Table 2. These were calculated by the use of thermodynamic fundamentals.

Table 2 Specific exergy values

Exergy flow	Symbol	Exergy value [J/g]
Exergy of the applied flow of heat	E_W	601.97
Exergy of the incoming fibre	$E_{fibre,in}$	0
Exergy of the incoming atmosphere gas	$E_{atm,in}$	1096.24
Exergy of the evolved gases	$E_{gas,out}$	10.42
The exergy of the leaving fibre	$E_{fibre,out}$	-14.25
Exergy of the outcoming atmosphere gas	$E_{atm,out}$	1668.71
Inner exergy loss	E_{inloss}	33.33

The transit adjusted exergy efficiency ζ is defined by following equation:

$$\zeta = \frac{E_P}{E_F} = \frac{E_{Abgas}}{E_{F,ein} + E_W} \qquad (2)$$

Therefrom results with the exergy values of table 3 a transit adjusted exergy efficiency of 1.73 %. Where by the exergy efficiency is equal to 72.21 %. The calculated exergy efficiency of 72.21 % indicates that the process of thermal conversion occurs almost ideal and the dissipation or internal exergy losses in comparison to the spent exergy are low. Further the exergy efficiency indicates that the process of thermal conversion proceeds very efficiently if the exhausted gas and heat flows are used exergetically. If the exhausted gas and heat flows are considered as waste and released in the environment, the exergy efficiency will decrease to zero. In this case, the process of thermal conversion will consist of pure dissipation.

4 CONCLUSION

The exergy efficiency is high because only a small part of the exergy is used for the thermal treatment of the fibre and the majority of exergy is used to heat the needed atmosphere. So the atmosphere has the greatest impact on the exergy efficiency in the process of thermal conversion. This is partly due to the oversized atmosphere gas flow compared to the treated fibre mass. If only the pure chemical process of fibre conversion is considered, the transit adjusted exergety efficiency should be used for the evaluation of the process. Here by the transit adjusted exergy efficiency describe how much exergy of the spent exergy is converted into usable gas exergy. Exergetically considered a high transit adjusted exergy efficiency is advantageous, but the focus of the thermal conversion lies in the production of carbon fibre with high performance and not in pursuing the aim of generating energy. Therefore, the interpretation of the adjusted transit exergy efficiency depends of the quality of the final fibre.

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