Conditions of Pyrolythic Processes in Multi Chamber Furnaces for Aluminium Recycling

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Abstract

After a coated aluminum product has reached the end of life cycle or laquered process scrap is generated it needs to be recycled in an economical, effective and ecological way. State of the art is the thermal removal of coatings and other organic fractions via treatment by pyrolysis. In modern multi chamber furnaces this step is realized in a separate pre-heating and melting compartment of the furnace. Although the weight fraction of coatings based on the mass is in the lower single digit percentage range, this is enough to decrease the efficiency of the recycling process and to reduce the quality of the generated aluminum melt. The incidence of aluminum losses can be traced back to the contained organic components, which lead to an aluminum burn off and thus increased dross production. Therefore the control of the pyrolysis step to remove organic fractions is essential for the aluminum quality and quantity.

Content of this work is the investigation of a typical situation in the aluminium remelting/recycling industry. The topic will be exemplary shown for painted beverage cans (production scrap) which is usually recycled in multi chamber furnaces. Another part of the current work is the downscaling of these terms of conditions to a lab-scale experimental setup in order to detect the optimal working range for pyrolysis in multi chamber furnaces. The significantly smaller lab-scale enabled rapid change of pyrolysis conditions and could be adjusted based on the settings of different multi chamber reaction conditions. Thus a comparison of different reaction processes is possible.

1 Introduction

Within the aluminum recycling industry large amounts of aluminum scrap usually are contaminated with organic material. This organic layer, for example, paint, oil or cellulose compounds, represent a significant carbon input into the process route of the aluminum recycling industry. It may have impact on the quantity and quality of the recycled aluminum. At the same time, the organic components could also be converted using a pyrolysis to potential energy resource, so that the fuel consumption and thus the recycling costs are reduced. The combination of a pyrolysis with simultaneous remelting of the scrap is achieved through the use of multi chamber furnaces. A ramp which is used for the pyrolysis step is in modern chamber furnace located inside the melting chamber.

The aim of this part of the current work is to investigate a more complete picture of the composition and amount of pyrolysis products through a variation of the oxygen concentration and scrap properties formed and to determine the exact duration of the pyrolysis process. The obtained analysis results are subsequently compared with each other and with those of a multi chamber furnace to show the potential for improvement.

2 Basics of thermal decomposition of organic material

In general the thermal decomposition of carbon material with and without oxygen is divided into three reactions. To make a distinction between these reactions called pyrolysis, combustion and gasification the oxygen number λ is defined. The oxygen number λ is the ratio of total air amount in the system to needed oxygen for stoichiometric total combustion. Table 1 shows an overview of process parameters and reaction products of thermic decomposition reactions [1, 2].

Table 1: Explanation of carbon decomposition regarding to the oxygen number λ [2]

	Process Parameter	**Reactions products (ideal)**
Combustion	$\lambda > 1$	CO_2, H_2O
Gasification	$0 < \lambda < 1$	CO, H_2
Pyrolysis	$\lambda = 0$	C_xH_y, C_{fix}
Autothermal Pyrolysis	$\lambda > 0$, T < 700 °C	C_xH_y, C_{fix}, CO_2, H_2O
Autothermal Gasification	$\lambda = 0.3$ to 0.5, T > 800 °C	CO, H_2, CO_2, H_2O

For the combustion of carbon containing material e.g. lacquers the oxygen number is bigger than one. So, that for the reaction of every mol carbon one or more mol of oxygen is available. Such combustion reactions generate a lot of heat energy as shown in equation 1.

$$C(s) + O_2(g) = CO_2(g) \qquad \Delta_R H = -393.5\,\frac{kJ}{mol} \tag{1}$$

In variance with the combustion the oxygen number range for gasification is between 0 and 1. Because of the low oxygen concentration (<< 1 %) in the pre-heating chamber of the furnace the leading carbon decomposition reaction is pyrolysis. Through considerable fluctuations of the oxygen level during the scrap charging step, combustion and gasification reaction are also possible. The interaction between these reactions is complex and not well known. Furthermore, the consequences of temporary increasing of oxygen concentration are unidentified for carbon decomposition reactions.

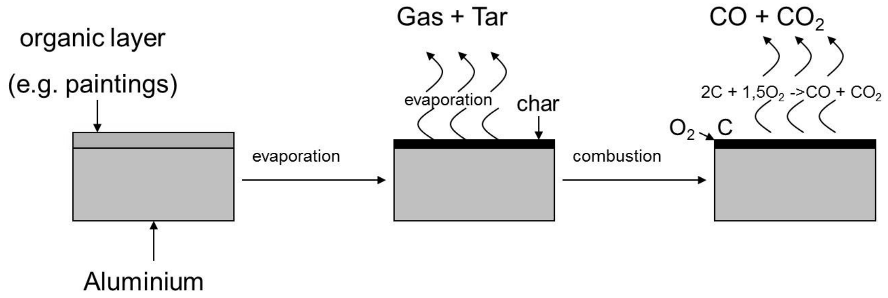

Figure 1: De-coating mechanism [3]

Figure 1 shows the reaction during an industrial pyrolysis process with the aim to reduce the total carbon amount of aluminum scrap. In the first step the organic components evaporate and form gas and tar. On the surface of the scrap remains a carbon-containing, tar residue. In the second step of the reaction on the surface remaining carbon reacts with the added oxygen and burn controlled to CO or CO_2 [3, 4].

$$\text{Organic(s)} = \text{Coke(s)} + \text{gaseous Components} \tag{2}$$

Equation 2 shows the overall pyrolysis reaction. Parallel to the gasification process at sufficiently high temperatures, an autothermal pyrolysis can be generated. In such a state simultaneously pyrolysis and combustion reactions are running. Before an autothermal pyrolysis can be achieved the pyrolysis process runs through several phases. Which reactions take place in these phases depends on temperature. These different reactions are shown below in Figure 2 [2, 5].

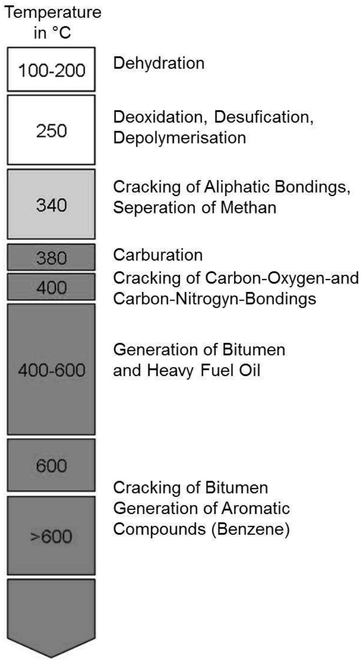

Figure 2: Pyrolytic decomposition of organic material depending to temperature [5]

3 Experiment

3.1 Feeding Material

For the experiments two different types of aluminium scrap are used. Oiled scarp and painted scrap coming from beverage can production, because of the dimensions of the used lab-scale pyrolysis reactor the scrap packages are cut into smaller blocks (60×60×200 mm). Figure 3 shows both scrap types in the lab-scale dimensions. On the cut site the inside block structure is fairly visible. It is obvious that the compacting process produces a large number of cavities inside of the block and thus an inhomogeneous heat conductivity.

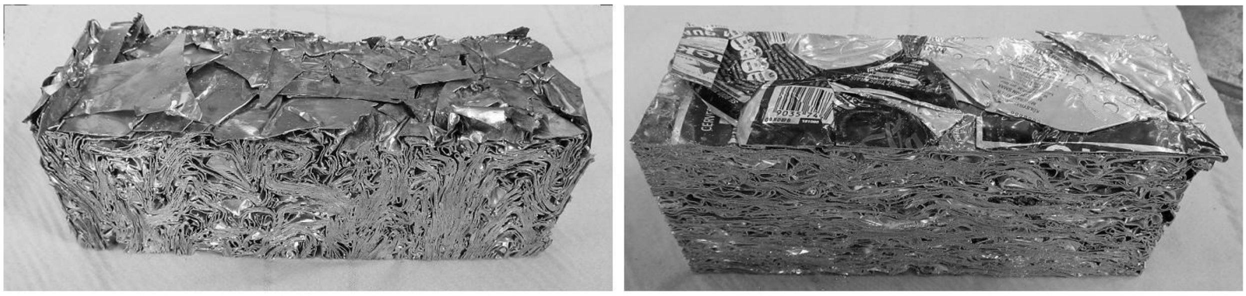

Figure 3: Feeding material

The different densities of the compacted scrap blocks are a result of various shapes of the scrap sheet. The painted blocks have an average weight of 840 g in different from oiled blocks with an average weight of 1050 g. This high deviation depends on the various degree of compaction. Another result of the different compaction is the higher amount of caverns inside of the painted material blocks. The medium weight is a result of aluminum and lacquer or oil amount. The percentage lacquer amount is located between 2 % and 4 %.

3.2 Equipment

In this study, only the carbon decomposition reaction step is simulated and there is no need for a meltdown in the first experiment step. Thus, there is the possibility to investigate the pyrolysed aluminum scrap after the experiment and draw a conclusion from the weight loss. A steal reactor is constructed for these experiments (Figure 4) to simulate the same conditions that can be found inside the melting chamber of a modern chamber furnace especially to adjust different atmospheres. To maintain a homogeneously distributed gas flow the reactor has a sieve as a false floor. A common resistance furnace is used for heating this reactor.

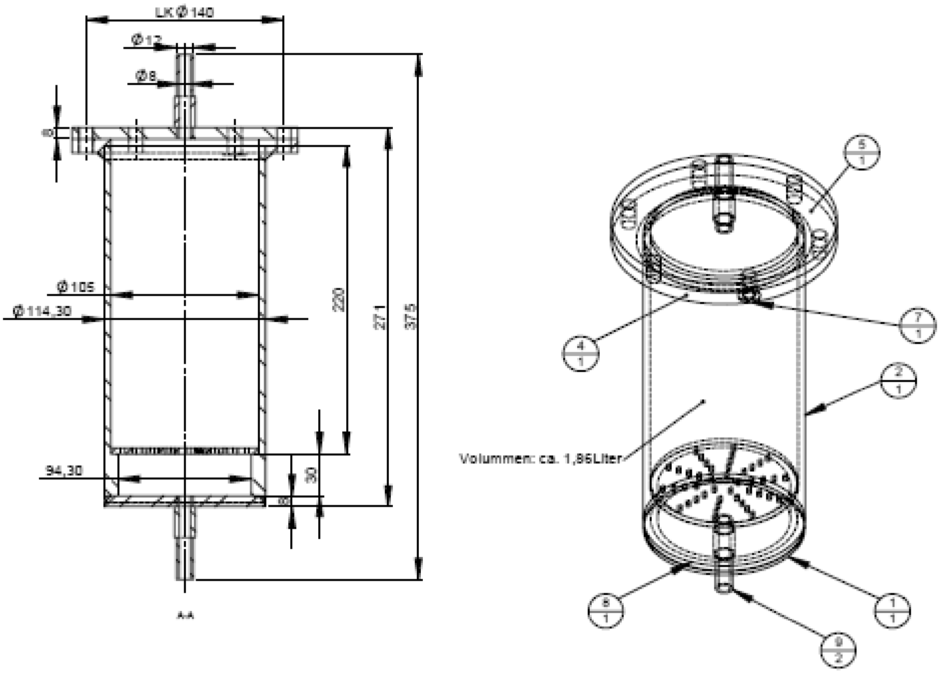

Figure 4: Used lab-scale reactor with false bottom

To separate the influence of oxygen from other atmosphere components it is possible to adjust different Argon, Oxygen ratios for the experiments. During the experiments CO, CO_2, O_2, C_xH_y and temperature are measured and logged. Figure 5 shows the complete experimental setup.

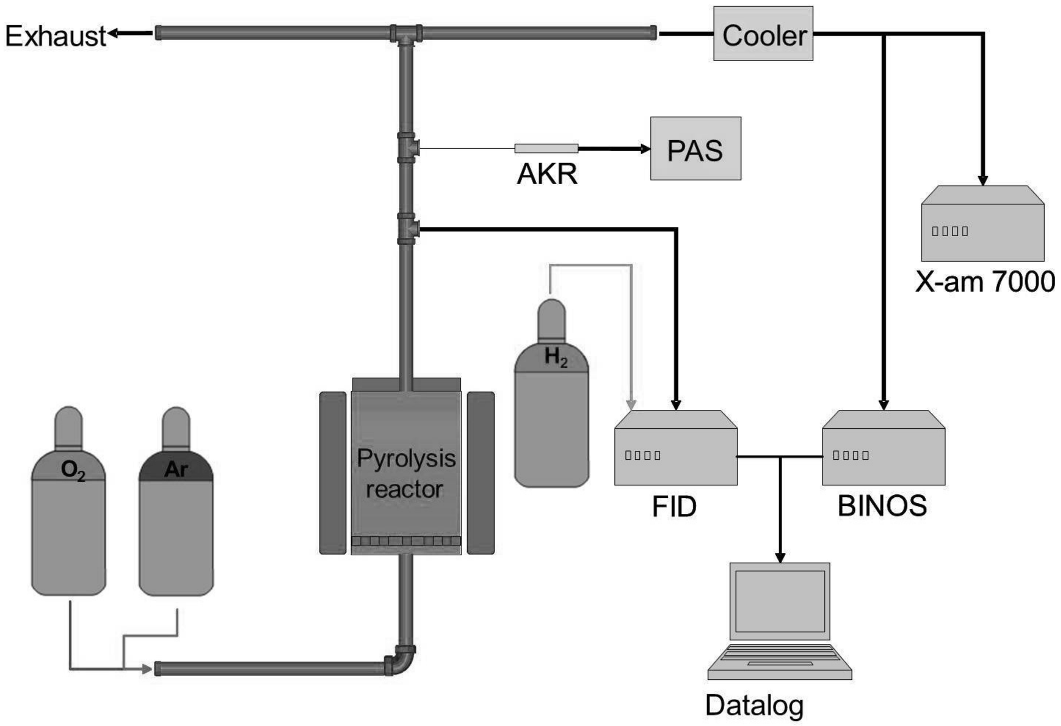

Figure 5: Experimental setup to analyze main gaseous reaction products

To analyse CO, CO_2 and O_2 a Binos 1001 with integrated Oxynos 100 and a X-am 7000 gas analysing devices are used redundant. Because of off-gas temperatures up to 350 °C a gas cooling system is used to protect these analysing devices. The FID (Flame Ionization Detector) detects hydrocarbons and other easily flammable components. The measured data are logged every 10 seconds.

4 Experimental results

In the first experiment campaign the influence of the oxygen level during the pyrolysis is investigated.

After performing 20 pyrolysis experiments in the IME lift resistance heated crucible oven at 600 °C, the following table is created. The weight before and after the carbon decomposition reaction of the used scrap blocks and the oxygen concentration of the individual experiments, which consists of the flow rates of argon and oxygen are illustrated.

Table 2: Results of the pyrolysis experiments

Trail No.	**Weight before pyrolysis [g]**	**Weight after pyrolysis [g]**	**Weight difference [g]**	**Difference [%]**	**Gasflow Ar [l/min]**	**Gasflow O_2 [l/min]**	**O_2 [%]**
V1	340.0	332.0	8.0	2.4	-	-	-
V2	861.0	841.0	20.0	2.3	20.0	1.2	0.4
V3	845.0	824.0	21.0	2.5	20.0	0.0	0.0
V4	866.0	847.0	19.0	2.2	20.0	2.0	3.4
V5	848.0	828.0	20.0	2.4	20.0	2.0	3.4
V6	842.0	823.0	19.0	2.3	20.0	1.5	1.0
V7	857.0	836.0	21.0	2.5	20.0	2.6	10.0
V8	1076.0	1068.0	8.0	0.7	20.0	0.0	0.0
V9	1019.0	1012.0	7.0	0.7	18.7	0.7	2.2
V10	833.0	812.0	21.0	2.5	18.2	2.9	10.0
V11	542.8	533.0	9.8	1.8	16.5	2.6	2.5
V12	598.8	586.2	12.6	2.1	15.2	1.5	2.1
V13	563.8	550.6	13.2	2.3	17.4	2.1	3.3
V14	561.4	550.9	10.5	1.9	14.5	0.0	0.0
V15	425.5	415.0	10.5	2.5	16.6	2.1	2.5
V16	542.8	531.7	11.1	2.0	16.6	2.1	2.4
V17	577.2	564.9	12.3	2.1	17.7	2.2	3.1
V18	562.5	550.7	11.8	2.1	17.7	1.9	1.0
V19	567.6	555.9	11.7	2.1	14.6	0.0	0.0
V20	572.6	559.6	13.0	2.3	20.0	3.1	1.2

In Table 2, all tests performed are listed. Tests 1 to 11 were performed with the original reactor configuration. In this configuration it was nearly impossible to charge the material in the hot reactor. The following experiments 12 to 20 were carried out in the modified version of the reactor. This modification allows to charge in the heated reactor without having a long influence of the normal atmosphere during charging. Furthermore, in experiments 8 and 9, material contaminated with oil is used. Experiment 1 is a test trial with a lower scrap amount and therefore it is not called in for the following analysis.

The comparison of weight losses of all experiments shows a percentage weight reduction between 1.8 to 2.5 wt. %. For this consideration only tests with fully painted scrap are used so that the tests do not involve experiment 8 and 9 in the result. These two experiments consistently show that it is to be expected in the pyrolysis of oiled scrap compared with painted scrap a reduced weight loss of 0.7 % by weight.

Figure 6 shows the input material before and after the experiment. The loss of the organic layer is clearly visible. The remaining contours are inter alia on metal oxides due that remain after pyrolysis on the aluminum.

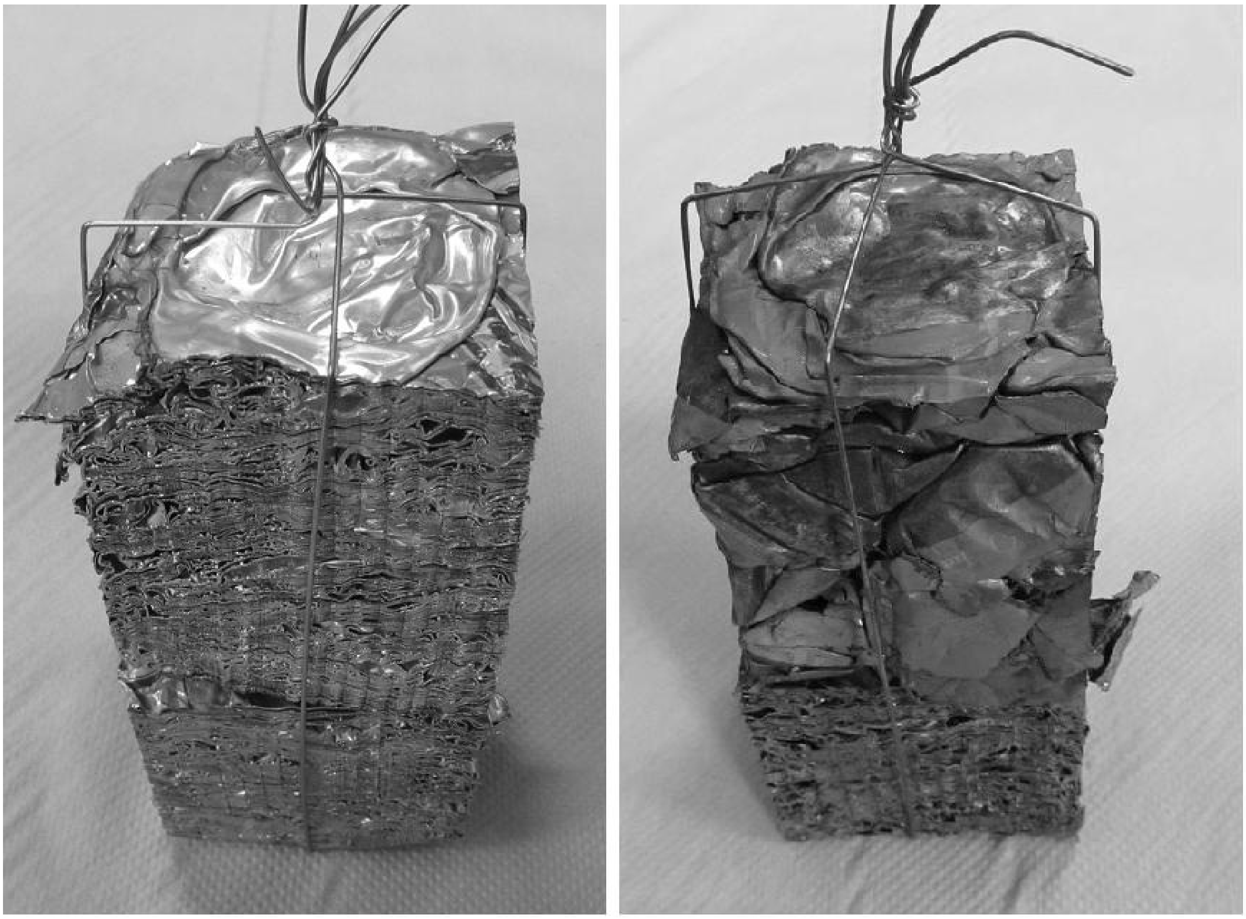

Figure 6: Scrap sample before and after pyrolysis experiment

After this first visual inspection of the pyrolysed scrap block the material along the block height is separated into seven sections. These cuts as well as those located within the block are shown in Figure 7.

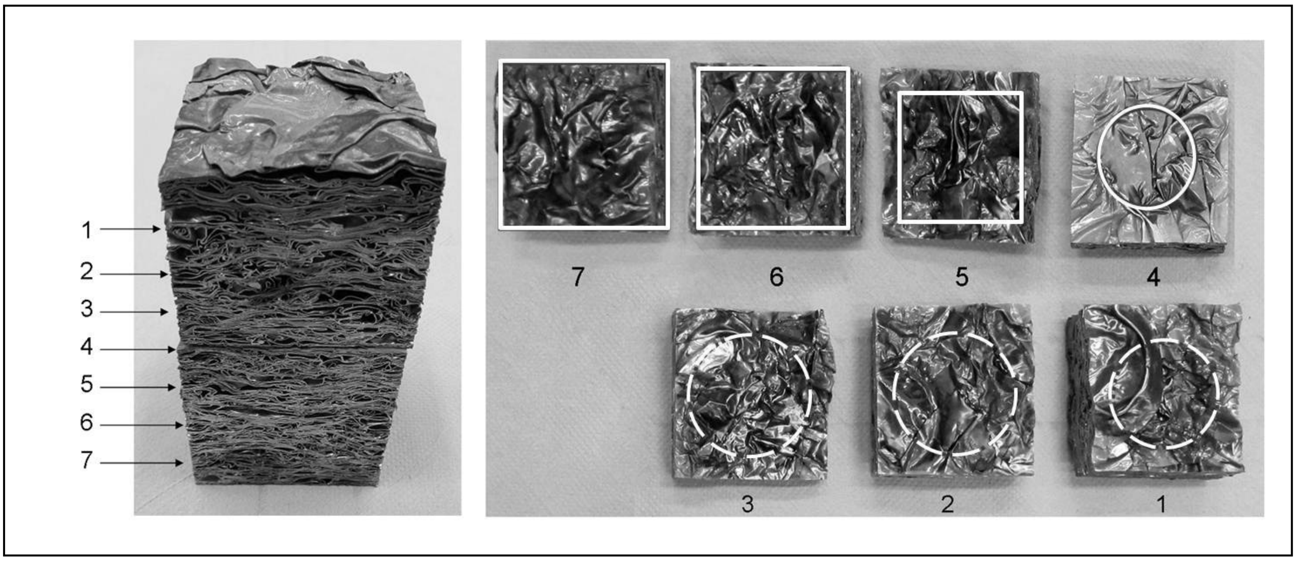

Figure 7: Divided scrap sample after pyrolysis experiment

The figure above shows contrary to the first visual assessment in Figure 6, that the entire organic amount is not pyrolysed completely. The dark paint residues inside the block are clearly visible. Which occurs in Figure 7 is indicated by white markings. It can be seen that the remaining organic residues are not evenly distributed across the block.

Especially in the lower block layers, carbon material is still present. This fact decrease slightly to the block centre. The sections 5 and 6 show a completely pyrolysed edge. At the surface layer 4, two block pieces lie on top of each other. Thus, there is a very good accessibility of the furnace atmosphere in the block centre, resulting in a high removal of organics. Only in the centre of this layer organic residues could be detected. On layers 1 to 3 within the centre area, low retention amounts of organic residues are found. The basic cause for the different pyrolysis grades in different scrap block areas is the gas flow between scrap layers. Although these scrap block samples have two open sides as a result of cutting the gas flow between the layers is not homogenous. It can be assumed that these effects are in the industrial process even higher as a result of block geometry and closed block structure.

Figure 8 shows a concentration over time diagram of the investigated gas components CO, CO_2, O_2 and C_{total}. This represents the results of the experiment 18, which is conducted with an oxygen concentration of 1 %. For a more detailed study the concentration curves are divided over the reaction time in three phases: start-, reaction- and “diffusion-phase”. The concept of diffusion is not to be understood according to its chemical definition, but rather should be made clear that organic material from inside the block take part at pyrolysis reactions with a certain time delay. Within this phase, the organic material at the block surface is already completely pyrolysed, consequently only organic material from the inner block takes part in this reaction step. These components must first leak from inside the block so that the shown decrease of concentration of CO, CO_2 can be explained. The transport of the organic compounds from the centre of the block is not completed within the trial period. Therefore, organic components remain inside the block.

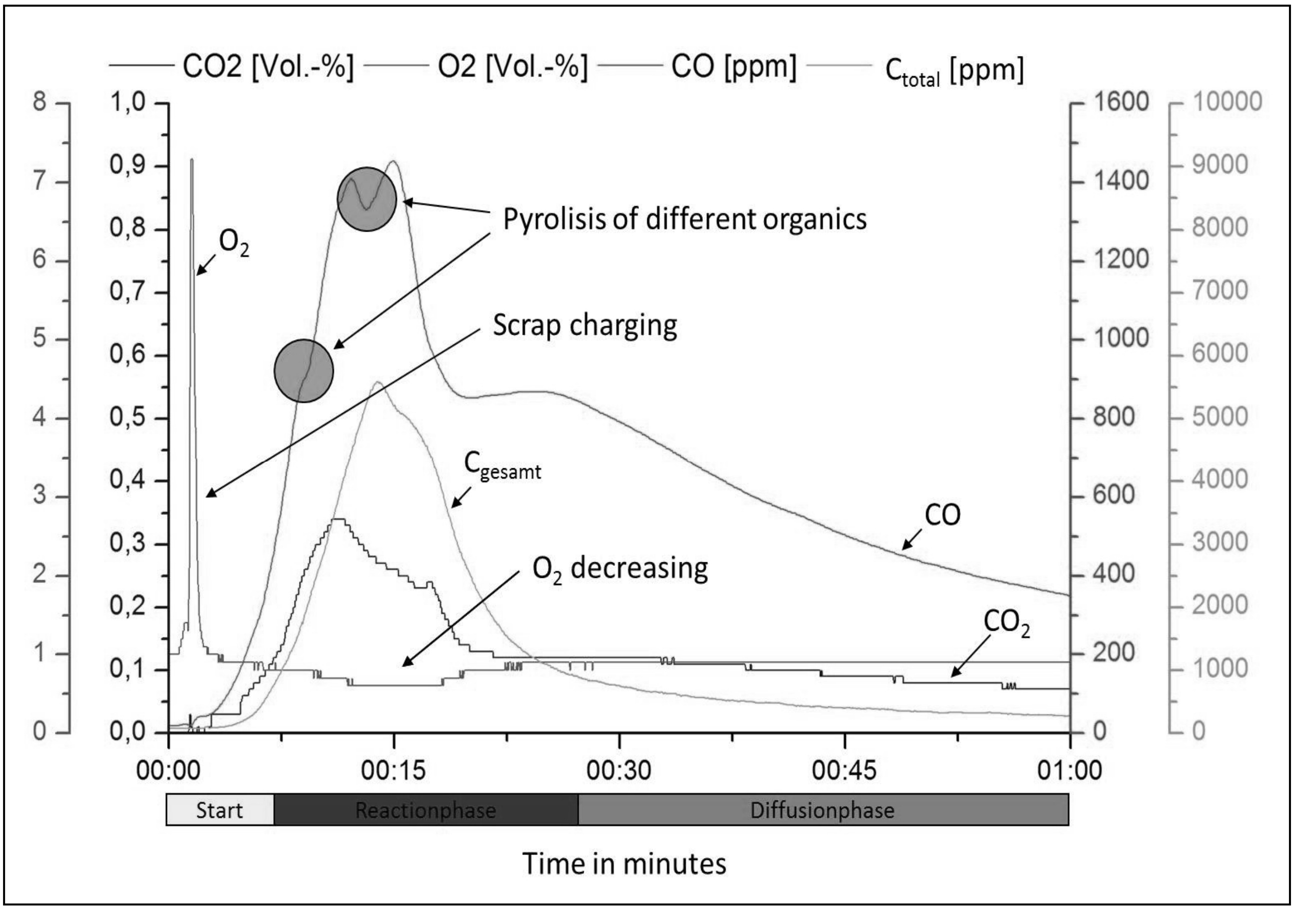

Figure 8: Typical concentration diagram during a pyrolysis experiment

The addition of the painted aluminum block can be recognized in the first 3 minutes in Figure 8. This explains the increase of oxygen concentration, during this short time the reactor lid is opened for charging and false air is entering the reactor. After resealing of the system from the ambient atmosphere the oxygen content drops to default 1.0 % O_2. The addition of scrap can be detected by a sharp increase of CO, CO_2 and C_{total} after a delay of one minute. The transition is defined in the reaction phase. The delay is due to the inertia of the measuring systems. During the reaction phase the concentration maxima of the studied carbon components are recognized, the maximum level is a result of the existing oxygen concentration. Especially the course of the CO concentration shows characteristics within the reaction phase. After nine minutes a temporary weakening of the concentration can be realized. Furthermore, the curve shows two local maxima after about 15 minutes, followed by a sharp drop of the CO concentration. Such irregularities can be passed at the beginning of the evaporation of other organics contained in the paint. These substances have a higher thermal stability, so that the pyrolysis of these materials is delayed. In a weaker form, this concentration sequence can also be found for CO_2 and C_{total} concentration.

5 Conclusion

The aim of the pyrolysis experiments, to transfer the pyrolysis conditions from an industrial chamber furnace to a lab-scale experiment and then to derive optimized the carbon decomposition conditions with modified atmospheres could be achieved in large parts of this work. Furthermore, the detected CO concentration profiles can be inferred from at least two other delayed reactions. This fact can be attributed to the different thermal stability within the organic components that do not participate to reach the required activation energy to the reaction. These observations can be confirmed by the evaluated CO_2 concentration profiles.

Considering weight loss the used scrap blocks have an average loss between 1.9 to 2.5 % for painted scrap and 0.7 % oil-containing material. This weight loss is independent of the oxygen supply and the detected concentration gradients. There is no impact to identify between the ratio of combustion, gasification and pyrolysis reaction respectively the oxygen number.

Such a statement leads to a contradiction, with increasing oxygen supply, the measured CO and CO_2 concentrations increases sharply and therefore an increased weight loss would be expected. This contradiction can be explained by the building of short-chain hydrocarbon compounds at low O_2 concentrations, which are not detected by the used instruments.

The current work shows that for the industrial multi chamber furnace process common charging time for of round about 30 min to increase the furnace output is too short for a complete pyrolysis process of baled thin sheet or foil scrap. The experimental work shows that the interval currently in use is not long enough to complete the pyrolysis of organic substances, which stick to the aluminum scrap. Coincidentally, the pyrolysis experiments show a maximum emission point after 15 minutes residence time in the pyrolysis reactor. In the following 15 minutes, a significant reduction of the investigated carbon compounds is observed, but not to the end of the reactions. This fact can be substantiated by an investigation of the scrap material after 30 minutes of pyrolysis that shows residues of organic close to the centre block regions.

The previously described situation leads to two consequences for the production of recycled aluminum in two-chamber furnaces. First, not all of the calorific value of the organic material adhering to the scrap will be used for the remelting process, since the residence time is not sufficient for this purpose. Thus, there is an increased natural gas consumption, which offset the amount not recovered pyrolysis. As a second consequence of the incomplete pyrolysis, the carbon input into the aluminum melt and the subsequent carbide formation is increasing. This entry can be reduced by continued pyrolysis. A reduction in carbon entry will have positive effects on the purity of the obtained secondary aluminum and reduce the inefficient formation of dross.

6 Outlook

In order to understand the distribution of carbon impact within the streams of a multi chamber furnace more precisely, further investigations will be carried out. The focus will be on determining real carbon mass flow through the dross and the recycled aluminum. In addition, the effects on melt purity and the amount of dross formation caused by the remaining carbon content on the scrap will be investigated. The current work shows that the pyrolysis process is still running when the scrap block is pushed under the melt. It is assumed that formed gases have a long contact time inside the melt. This gas/liquid reaction will increase the dross formation. A longer pyrolysis time could prevent these effects. To separate these effects gas injections experiments are running to investigate the influence of different pyrolysis gaseous products in aluminum melts.

However, to find the best way between complete transformation of organic material into furnace atmosphere and a high furnace performance is the challenge.

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