CHEMICAL ENGINEERING TRANSACTIONS
VOL. 88, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš

ISBN 978-88-95608-86-0; **ISSN** 2283-9216

DOI: 10.3303/CET2188021

Greening Tin Metallurgy with Renewable Biocarbon Reducing Agents

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The article discusses the possibility of a new method for processing tin-containing raw materials using a renewable carbon source - rice husks. A review of the literature on this topic showed the absence of publications on the possibility of using unconventional reducing agents in tin metallurgy. The work is devoted to filling the gap in the study of the possibility of using rice husks as a reducing agent in tin metallurgy. The process of pyrolysis of rice husks and reduction of tin oxide using rice husks were compared with traditional reducing agents, coal and coke. Heating was carried out in an inert atmosphere (argon). Thermal effects were studied using thermogravimetric analysis and differential scanning calorimetry. The optimal heating rate (5 °C/min) with the maximum decomposition of rice husks (up to 82 %) was found experimentally. It was found that the reduction of SnO_2 with coal and rice hulls begins already at ≥ 800 °C, while interaction with coke does not occur even at 900 °C and above. Rice husks have been proven a promising reductant for SnO_2.

1. Introduction

Tin is one of the metals that determine the development of human civilization. Tin is used in many industries: food, chemical, electronics, as well as in the manufacture of batteries. The price for refined tin as of April 19, 2021 was US$ 27,940/t (LME, 2021). In 2020, 270 kt of refined tin were produced worldwide. The leaders in tin production are China - 81 kt, and Indonesia - 66 kt. World tin reserves for 2020 are 4.3 Mt (USGS, 2021). Almost half of the total tin production goes to electronics. And only 17 % of this volume is recycled and returned to production (ITA, 2020). In general, as of February 14, 2020, out of the total volume of tin produced in the world, only about 16 % is secondary tin (ITA, 2020).

In Kazakhstan, as in the rest of the world, much attention is paid to finding ways to recycle tin (Sapinov et al., 2020). However, it is obvious that ore raw materials remain the main source of tin production. Therefore, it is very important to make traditional tin production technologies more efficient in terms of reducing energy costs and harm to the environment. In the Republic of Kazakhstan there are also reserves of tin ore suitable for development from an economic point of view. The Kazakhstani tin deposit Syrymbet is included in the 10 most significant deposits according to the assessment of the International Tin Association (ITA, 2020). Currently, work is underway to adjust the production of tin concentrate at the Syrymbet deposit. The main mineral in the extraction of tin from mineral raw materials is cassiterite (SnO_2) (López et al., 2018). To obtain tin from cassiterite, pyrometallurgical reduction methods are traditionally used. Low-sulfur coals and, more rarely, coke are used as a reducing agent (Wang, 2016). Since coal is a non-renewable fuel resource, such processes increase the carbon footprint and harm the environment (NG, 2019).

For Kazakhstan, environmental problems are one of the most important, since many metallurgical and energy industries are concentrated in the Republic. One of the solutions to problems with environmental pollution is the use of various renewable carbon sources in metallurgical production. These include straw, rice husks, algae, etc. About 500 kt of rice are grown annually, while the mass of rice husk is 30 wt. % of the mass of dry grain (DK, 2019). A promising direction in solving issues of utilization of rice husk is its use as a carbon source in the reduction of oxides metals. It is known that carbon is the basis of the organic part of rice husk - lignin, cellulose,

Paper Received: 20 May 2021; Revised: 8 August 2021; Accepted: 11 October 2021
Please cite this article as: Sapinov R.V., Sadenova M.A., Kulenova N.A., Suyundikov M.M., 2021, Greening Tin Metallurgy with Renewable Biocarbon Reducing Agents, Chemical Engineering Transactions, 88, 127-132 DOI:10.3303/CET2188021

and hemicellulose (Huang and Lo, 2019). Due to the high (up to 54 %) content of volatile substances (Maksum et al., 2018), rice husks can be an effective reducing agent for metal oxides. The volatiles released during pyrolysis of rice husks contain up to 41 % carbon monoxide, 15 % hydrogen, and up to 15 % methane (Gautam and Chaurasia, 2019). It is known that carbon monoxide plays an important role in the reduction of metal oxides (Dang et al., 2018), and methane is an effective reductant of tin oxide (Ha et al., 2017). However, as a result of the review, it turned out that today there are practically no works devoted to studying the possibility of using rice husks and other renewable carbon sources in tin metallurgy. In this regard, the purpose of this article is to study the possibility of using rice husks as a reducing agent for tin oxide (SnO_2). This can improve the environmental friendliness of tin metallurgy, and offer a solution for the disposal of rice husks. For this, the processes of pyrolysis of rice husks and the possibility of reducing tin oxide using rice husks and traditional reducing agents were studied. At the first stage, thermodynamic modeling of the reduction reactions of tin oxide using volatiles (CO, H_2) was carried out. Further, the mechanisms of the process of pyrolysis of rice husks at different heating rates were investigated. This made it possible to select the optimal heating mode for the reduction of SnO_2, with the maximum release of volatiles. The study of the kinetics of pyrolysis processes was based on the regularities given in the work of Mong et al., (2020). Further, the heat effects of the reduction of SnO_2 using rice husks and traditional reducing agents (coal, coke) were investigated.

2. Investigation of the thermal effects of the process of pyrolysis of rice husks and reduction of tin oxide using various reducing agents

Materials and methods

For the study, coals from the Shubarkol deposit, metallurgical coke, rice husks and SnO_2 of laboratory purity were taken. All reducing agents are of Kazakhstani origin. All experiments were carried out on the basis of D. Serikbayev East Kazakhstan Technical University (EKTU, www.ektu.kz/?lang=en). Thermodynamic modeling was carried out using the HSC 9 program (OR, 2021). To determine the chemical composition (Table 1) by the spectral method, an ICP-MS 7500cx inductively coupled plasma mass spectrometer (Agilenttechnologies, USA) was used. To study the phase composition, an X'Pert PRO X-ray diffractometer manufactured by PANalitical was used.

2.1 Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) equipment (METTLER TOLEDO Switzerland) was used to carry out TGA and DSC analysis of the pyrolysis reaction of reducing agents and the thermal effects of SnO_2 reduction. For each experiment, the weighed portion was placed in a crucible, which was lowered into the reaction chamber. To analyze the pyrolysis reaction of rice husks, a 3 mg sample was heated from 25 °C to 1000 °C at a heating rate β equal to 5 °C/min, 10 °C/min, 20 °C/min, and 30 °C/min. Heating was carried out in a flow of argon (purity: 99.8 %) supplied at a flow rate of 40 mL/min. For each experiment, the study of the reduction reaction of SnO_2 with various reducing agents, a weighed portion of a mixture of SnO_2 and a reducing agent was placed in a crucible, which was lowered into the reaction chamber. The amount of the reducing agent was stoichiometrically twice that required for the complete reduction of SnO_2. When a peak appeared in the diagram, heating was stopped, and the material was sent for X-Ray Diffraction (XRD) analysis to study the resulting reaction products. Heating was carried out up to 900 °C.

2.2 The theory of kinetics of the pyrolysis process

To study the processes and patterns occurring during the thermal decomposition of reducing agents, it is necessary to know the kinetics of the processes. To describe the decomposition rate of rice husks, the formula for the conversion of the sample mass (α) was taken (Mong et al., 2020). The level of conversion of the sample mass (α), which will allow us to judge the intensity of the pyrolysis process, is calculated by the formula (1).

$$\alpha = \left(\frac{m_i - m}{m_{i-m_f}}\right) \tag{1}$$

Where m is the instantaneous mass, m_i is the initial mass before the experiment, and m_f is the final remaining mass.

3. Results and discussion

3.1 Thermodynamic modeling of tin oxide reduction reactions

The HSC 9 software was used to determine the Gibbs free energy (ΔG) of the SnO_2 reduction reactions. Possible reactions of reduction of SnO_2 with carbon, hydrogen and CO have been studied. Temperature range 0 °C to 1000 °C. Step 100 °C. Reduction with carbon is theoretically possible from t = 700 °C (ΔG = -22.914

kJ/mol). This correlates with the data of the study by Mitchell A.R. and Parker R. H., (1988). Reduction with CO is theoretically possible from t = 100 °C (ΔG = -1.291 kJ/mol). Hydrogen reduction is possible from t = 600 °C (ΔG = -5.68 kJ/mol). This is consistent with the data of Kim et al., (2011). Therefore, it can be assumed that in the presence of volatile substances, the reaction can begin at lower temperatures.

3.2 Study of the thermal effects of pyrolysis of reducing agents in a neutral atmosphere

Before carrying out TGA and DSC analysis of the reducing agents, their main characteristics were established (Table 1).

Table 1: Characteristics of reducing agents

Reducing agent	Moisture, %	Ash content, %	Volatile, %	Content C, %
Coal	10.3-15.3	2.2-3.12	41.5-46.9	51-55
Coke	2.8-3.2	12.8-14.6	0.7-1.1	79-85
Rice husks	2.4-4.8	10.3-15.1	38.7-45.9	32.2-38.6

The elemental composition of rice husks is shown in Table 2. It can be seen that rice husks contain a large amount of carbon (35.4 wt. %) and oxygen (43.7 wt. %), which form the basis of the organic part of rice husks (cellulose, hemicellulose and lignin).The content of carbon and hydrogen may differ slightly (Balasundram et al., 2020), which is probably related to the region of rice cultivation.

Table 2: Elemental composition of rice husks (wt. %)

Element	C	H	O	N	K	Si	Ca	Mg	Al
	35.4	5.6	43.7	1.16	0.86	7.8	0.10	0.11	0.06

Figure 1a shows graphical representations of TGA analyzes carried out in an argon atmosphere, the process of pyrolysis of rice husks, at heating rates β equal to 5 °C, 10 °C, 20 °C and 30 °C/min. The experiment showed that for all heating rates there are characteristic zones that can be conditionally divided into three parts. These findings correlate with the study by Mong et al., (2020). The 1st stage, the weight loss of the rice husk sample at all heating rates is observed at temperatures from 47 °C to 153.5 °C, weight loss ≈ 2 % (Table 3). At this temperature, the evaporation of hygroscopic moisture, and the lightest volatile fractions contained in rice husks, takes place. The conversion of rice husks is insignificant due to the low energy of the process, and is equal to α = 0.02 for all β. The 2nd weight loss occurs in the range from 153.5 °C to 418.3 °C and amounts to 41 % for β = 20°C/min. Such a significant weight loss is explained by the fact that decomposition reactions of cellulose and hemicellulose take place at these temperatures (Chong et al., 2019). Figure 1b shows the heat peaks located in the range of decomposition temperatures of hemicellulose and cellulose for β = 5 °C/min.

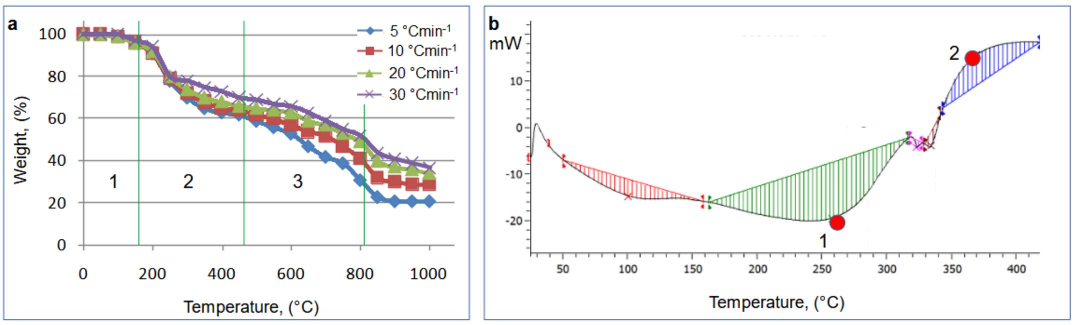

*Figure 1: **a** TGA analyzes carried out in an argon atmosphere, the process of pyrolysis of rice husks,**b** thermal effects of decomposition of hemicellulose and cellulose for β = 5 °C/min.*

Since hemicellulose has a lower degradation temperature, it can be assumed that peak 1 shows the degradation reaction of hemicellulose, and peak 2 shows degradation of cellulose. At higher temperatures, decomposition of inorganic substances begins (Mong et al., 2020).

Table 3: Reducing agent characteristics

Stage 1				Stage 2			Stage 3		
β	T_S	T_F	α	T_S	T_F	α	T_S	T_F	α
5°C/min	47 °C	153 °C	0.02	153 °C	418 °C	0.38	542 °C	859 °C	0.82
10°C/min	37 °C	168 °C	0.02	156 °C	425 °C	0.34	549 °C	861 °C	0.75
20°C/min	44 °C	194 °C	0.02	193 °C	431 °C	0.41	562 °C	875 °C	0.76
30°C/min	51 °C	207 °C	0.02	214 °C	467 °C	0.36	598 °C	904 °C	0.79

T_S temperature of the beginning of the thermal effect, T_F temperature of the end of the thermal effect

With an increase in temperature, the rate of mass loss shifts with an increase in the heating rate to the region of higher temperatures. So, at β = 5 °C/min, the temperature of the beginning of the thermal effect (T_S) was 153 °C, and the temperature of the end of the thermal effect (T_F) 418 °C. At β = 30 °C/min, the temperature of the beginning of the thermal effect (T_S) was 214 °C, and the temperature of the end of the thermal effect (T_F) was 467 °C. This can be explained by the thermal retardation of heat transfer from the environment to the sample (Mong et al., 2020). At the third stage of weight loss, a higher level of material conversion (0.82) can be noted at a heating rate β equal to 5 °C/min. Thus, this heating rate is the most effective from the point of view of pyrolysis and the production of volatile substances, effective reductants of SnO_2. Next, we studied the thermal effects of the reduction of SnO_2 with a heating rate of 5 °C/min. To study the nature of the peaks, additional experiments were carried out; after each peak, the experiment was interrupted, and the reaction products were subjected to X-ray phase analysis, thus, the qualitative composition of the reaction products was prepared (Table 3).

3.3 Study of the thermal effects of the reduction of tin oxide in a neutral atmosphere

Figure 2 shows graphical images of DSC and TGA analyzes the process of tin oxide reduction by coal from the Shubarkol deposit in an argon atmosphere. The phase composition of the products of the peaks of the SnO_2 reduction reactions is presented in Table 4.

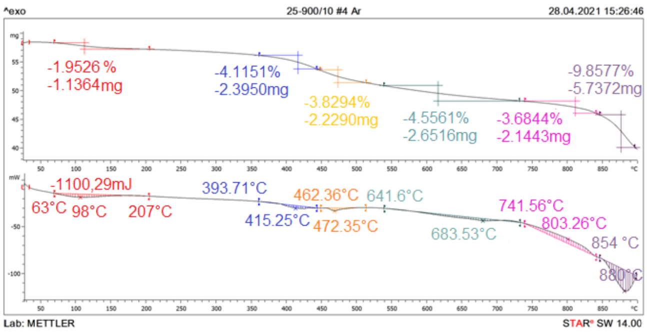

Figure 2: Graphical images of DSC and TGA analyzes carried out in an argon atmosphere, reduction of tin oxide using coals from the Shubarkol deposit

The graphs show that the weight loss of a sample of coal and SnO_2 is observed at temperatures from 63 °C to 207 °C (first stage, weight loss ≈ 1.95 %). At this temperature, the hygroscopic moisture contained in the coal evaporates and heat is absorbed. Reduction of SnO_2 does not occur. An endothermic reaction takes place from a temperature of 393 °C to 740 °C. Evidently, volatiles are released at this time. Hitch weight loss ≈ 13 %. The reduction of SnO_2 does not occur, and then an exothermic reaction is observed from 741 °C to 900 °C. SnO_2 is reduced to Sn (Table 3). Hitch weight loss ≈ 14 %. Figure 3a shows graphical images of DSC and TGA analyzes carried out in an argon atmosphere, reduction of SnO_2 using metallurgical coke. Moisture in coke and volatiles are practically absent. Weight loss in the first stage is 0.16 %, at temperatures from 331 °C to 495 °C. At this temperature, an endothermic reaction is observed. It can be seen from the graphs that a noticeable loss of sample weight is observed only starting from a temperature of ≈ 495 °C. The second stage is from 495 °C to 610 °C, weight loss ≈ 1.12 %. An exothermic reaction is observed. The third stage from a temperature of 745 °C to 900 °C, an exothermic reaction is observed. Hitch weight loss ≈ 2.4 %. The reduction of SnO_2 does not occur in any of the temperature regions. Apparently, conditions are not created for the formation of a sufficient amount of CO. Figure 3b shows graphic images of DSC and TGA analyzes carried out in an atmosphere of air, reduction of SnO_2 using rice husks.

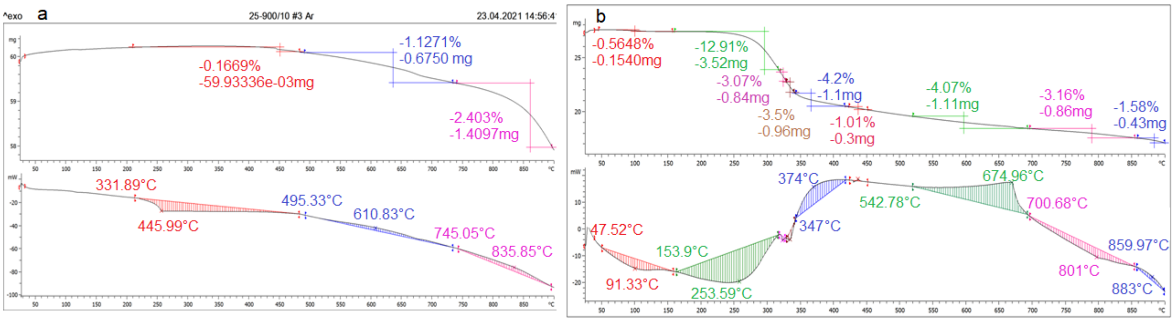

Figure3: a DSC and TGA analyzes of the reduction of tin oxide using metallurgical coke, b DSC and TGA analysis, reduction of tin oxide using rice husks

Table 4: Qualitative composition of reaction products

Reducing agent	Temperature Peak, t °C	Weight loss, %	Reaction product
Coals	98	1.95	SnO_2
	415	4.1	SnO_2
	472	2.8	SnO_2
	683	4.3	SnO_2
	803	3.7	Sn, SnO_2
	880	10	Sn
Coke	445	0.16	SnO_2
	610	1.2	SnO_2
	835	2.4	SnO_2
Rice husks	91	0.56	SnO_2
	253	20	SnO_2
	374	4.2	SnO_2
	674	4	SnO_2
	801	3.1	Sn, SnO_2
	883	1.6	Sn

It can be seen from the graphs that the first weight loss of the sample is observed at a temperature from 50 °C to 153 °C (first stage, weight loss ≈ 0.56 %). At this temperature, the evaporation of hygroscopic moisture contained in rice husks and light volatiles occurs. The second weight loss of the sample is observed at temperatures from 153 °C to 347 °C. (≈ 20 %). Endothermic reactions take place from a temperature of 50 °C to 347 °C. It is obvious that at this time there is an increase in the energy of the sample material, and its decomposition begins. The third weight loss of the sample is observed at temperatures of 347 °C to 420 °C (≈ 4.2 %). The fourth weight loss of the sample is observed at temperatures from 542 °C to 700 °C (≈ 4 %). Exothermic reactions take place from 347 °C to 700 °C. The fifth weight loss of the sample is observed at temperatures of 700 °C to 859 °C. (≈ 3.1 %). SnO_2 is being reduced. The reaction is endothermic. The sixth weight loss of the sample is observed at temperatures from 859 °C to 900 °C. (≈1.6 %).

4. Conclusions

In this article, for the first time, the possibility of reducing tin oxide using renewable sources such as rice husks was studied. At the first stage, using the HSC 9 program, modeling of the main redox reactions was carried out. Modeling the reactions showed that the reduction of SnO_2 with carbon monoxide is theoretically possible at 100 °C, and with hydrogen at 600 °C. At the second stage, the process of pyrolysis of rice husks at various speeds was studied. The most complete decomposition was obtained at a heating rate of 5 °C/min. At the third stage, a comparison was made of various reducing agents by heating a mixture of various reducing agents and tin oxide in an argon atmosphere. Reduction of tin oxide using coal and rice husks began at temperatures above 800 °C. There was no reduction of tin oxide by coke upon heating to 900 °C. Obviously, the reduction of SnO_2 with coke requires higher temperatures and air supply to form CO. Heating a mixture of various reducing agents and SnO_2 showed a total weight loss of 31 % for rice husks, 26 % for coal, and 3.5 % for coke. This indicates a greater yield of volatile (active reducing agents) in rice husks. Due to this, the use of rice husks as a reducing agent for tin oxide looks promising. The next stage of work will be to study the possibility of producing tin metal from the ore of the Syrymbet deposit using rice husks.

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