A Thermodynamic & Sustainability Assessment of PCB Recycling through the Secondary Cu Smelting Process

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ABSTRACT

This study presents a comprehensive thermodynamic optimization and sustainability analysis of the secondary copper smelting process for Waste Printed Circuit Board (WPCB) recycling. The study investigates various scenarios with different proportions of WPCB in the input stream, ranging from 0% to 100%. Through thermodynamic modeling using FactSage version 8.1, the optimization process is conducted in three stages. The results of the thermodynamic modeling indicate that the best-case scenario for WPCB recycling is achieved with a 40% proportion of WPCB in the input stream. This case exhibits a maximum copper recovery of 99.93% while minimizing the formation of other waste. In addition to the thermodynamic analyses, environmental factors such as the carbon emission index and resource utilization efficiency are studied. The 40% WPCB recycling case exhibits a resource utilization efficiency of 93.055% and a carbon emission rate of 0.133. The present investigation highlights the significant benefits of a 40% WPCB recycling scenario through a secondary copper smelting process in terms of base metal recovery and energy efficiency, thus emphasizing its potential for sustainable PCB waste management and resource utilization.

INTRODUCTION

Pyrometallurgical processes utilize elevated temperatures to extract metals from various sources. These processes encompass a range of techniques such as dressing, incineration, furnace-based smelting, sintering, melting, and high-temperature reactions in a gaseous phase. The primary objective is to recover common metals and precious metals from different wastes (Wu et al., 1993). During smelting, e-waste is introduced into a high-temperature furnace, often integrated with a base metal production process such as copper, lead, or zinc smelting. In this process, the base metal acts as a medium for collecting valuable metals such as gold, silver, platinum, and palladium (Ghodrat et al., 2017). Over the past few decades, pyrometallurgical methods have been extensively employed to recover metals from diverse waste materials.

Processes like smelting in furnaces, incineration, combustion, and pyrolysis are commonly used to recycle electronic waste (e-waste). Numerous studies have documented substantial metal retrieval achieved through pyrometallurgical methods; however, the prominent drawbacks of these processes include their high cost, substantial energy requirements, and the emission of hazardous fumes into the environment (Chauhan et al., 2018). It should also be noted that advanced smelters and refineries have proven effective in extracting valuable metals while also isolating hazardous substances. During the pyrometallurgical process, waste electrical and electronic equipment (WEEE) is subjected to high temperatures and combined with fluxes such as copper slag or various salts (e.g., NaOH) to facilitate the formation of slag. The resulting molten WEEE containing valuable metals is then brought into contact with a molten metal pool, where the valuable metals dissolve and accumulate. This molten metal pool acts as a collector metal. (Syed, 2012)

Printed circuit boards (PCBs) play a critical role in electronic and electrical equipment (EEE) and form the backbone of modern electronic and electrical infrastructure (Liu et al., 2016). The PCBs are made up of glass fiber-reinforced epoxy and various metallic materials, including valuable metals (Choubey et al., 2015; Gu et al., 2016). WPCB represents a significant reserve of recyclable resources (Holgersson et al., 2017), with the concentration of metals, especially precious metals, exceeding that of primary minerals, highlighting the economic advantages of recyclability (Cucchiella et al., 2016). Moreover, the WPCBs recycling positions them as valuable urban mineral resources (He and Duan, 2016), underscoring their significance in the context of sustainable resource management.

PCBs are crucial components in electronic products, but their recycling presents challenges. PCBs contain precious metals and hazardous elements, requiring proper management to minimize environmental and health risks. These boards consist of materials like phenolic/cellulose paper or epoxy, woven glass fiber, and various metals such as copper, tin, and lead (Ning et al.,2018) Valuable precious metals like gold, nickel, platinum, palladium, and silver can be recovered from WPCBs, making them economically attractive for recycling (Lu, 2016). However, it is essential to recognize that certain chemical elements in circuit boards, such as bromine, antimony, cadmium, and lead, exceed their natural crust composition, posing potential environmental and health risks. (Chauhan et al., 2018). Arensen et al., 2013 utilized NaOH salt during the melting of waste PCB from mobile phones and computers to increase the recovery of copper. Christian Hagelüken, 2006 reported that loss of copper during the recycling process will make up for 7 to 42% value loss. ISASMELT process for reductive smelting of e-waste has been extensively studied to understand the major challenges such as control of slag composition, temperature, fume formation due to Zn, Pb and Sn (Stuart et al., 2023). Therefore, efficient recycling processes towards maximizing the base metal recovery as well as minimizing the environmental impact are essential for sustainable e-waste practices. In the present study, thermodynamic simulations are adopted to identify the optimum condition for recycling WPCB towards maximum base metal recovery and minimum environmental impact.

METHODOLOGY

FactSage Simulation

The present study investigates the material flow while processing copper scrap and WPCBs in the black copper smelting process. The chemical thermodynamic modeling and process flowsheet simulations were employed to generate data for calculations. The thermodynamic calculations were conducted using the FactSage thermochemical package (version 8.1), allowing for accurate process modeling. Thermodynamic modeling and calculations offer a comprehensive approach to understanding the behavior of copper scrap and WPCBs during the black copper smelting process. Varying e-waste and copper scrap proportions (varied from 0 to 100) were utilized as input parameters to simulate the black copper smelting process. Other input material streams are Coal, FCS Slag, enriched air, and flux. The proportion of flux used in the simulation is maintained constant, as described in the previous work (Ghodrat et al., 2017) for 12 tons of charge materials. The detailed composition of various input streams considered in thermodynamic modeling can be found in the annexure (Ghodrat et al., 2017). The composition of black copper formed in the different cases is presented in the annexure. It should be noted that there are no solid phases observed in both the output streams (molten black copper and slag) under optimized conditions. By examining different scenarios, the research aimed to gain insights into the material flow during different percentages of e-waste recycling through the secondary Cu smelting process. The results obtained from this study contribute to the knowledge base surrounding the recycling and recovery of valuable metals from electronic waste. The study also informs potential process improvements for sustainable and efficient resource utilization. Different proportions of the input stream are presented in Table 1.

Table 1: List of basic input streams considered for FactSage simulation (Ghodrat et al., 2017)

WPCB recycling (%)	WPCB (tonne)	Copper scrap (tonne)	FCS slag (tonne)
0	0	12	0.42
10	1.2	10.8	0.42
20	2.4	9.6	0.42
30	3.6	8.4	0.42
40	4.8	7.2	0.42
50	6	6	0.42
60	7.2	4.8	0.42
70	8.4	3.6	0.42
80	9.6	2.4	0.42
90	10.8	1.2	0.42
100	12	0	0.42

Thermodynamic Optimization

A fixed input quantity of 12 tonnes comprising various proportions of e-waste and copper scrap, as detailed in Table 2, was used as input to determine the optimized process parameters. The thermodynamic optimization has been done stage-wise, as listed below, Stage 1: Identification of coal-air ratio for maximum Cu recovery and minimum residual solid carbon in the product stream.

Stage 2: Identification of optimized process temperature based on maximum liquid slag formation.

Stage 3: Identification of the optimum amount of flux (lime) addition to enhance liquid slag formation and suppress solid slag formation.

In the first stage of thermodynamic optimization, the coal-air ratio was systematically varied, keeping all other input streams constant. It should be noted that the WPCB in the input stream also contains carbon as a part of plastics. Consequently, the optimal amount of coal addition must be determined for maximum recovery of base metal copper while minimizing the formation of solid carbon residue in the output stream.

In the second stage, the process temperature was optimized to enhance the formation of a maximum quantity of liquid slag to facilitate the efficient separation of molten metal and slag. In this stage, the temperature was varied within a specified range, and the temperature at which the weight percentage of liquid slag reached its peak was identified as the optimal temperature.

In the third stage, the optimal amount of flux (lime), was determined to promote the formation of liquid slag in the output stream. The objective was to eliminate the formation of solid slag in the output stream and maximize the quantity of liquid slag, thereby facilitating the separation of metal and solid slag. Lime addition for each case was carefully selected to have minimum slag viscosity, further aiding the separation process.

The distribution coefficient of the element is a measure that compares the amount of element present in black copper (metal phase) to the combined amount of metal found in slag, exhaust gas, and metal dust (waste streams). It provides valuable insights into the distribution of valuable metal between these useful products and waste streams.

$$\mathbf{Distribution\ coefficient} = \frac{\mathbf{weight\ of\ element\ i\ in\ black\ Cu\ (kg)}}{\mathbf{weight\ of\ element\ i\ in\ slag{+}dust{+}gas\ (kg)}} \quad (1)$$

Metal recovery of element ‘i’ is defined as a measure that compares the amount of element ‘i’ present in black copper (metal phase) to the amount of element ‘i’ found in input streams.

$$\mathbf{Metal\ recovery} = \frac{\mathbf{weight\ of\ element\ i\ in\ black\ Cu\ (Kg)}}{\mathbf{weight\ of\ element\ i\ in\ input\ streams\ (Kg)}} \quad (2)$$

Sustainability Assessment

The environmental implications associated with current smelting systems have become increasingly important due to stricter emission targets and escalating energy costs. The present study's primary focus was to examine three indicators from environmental responsibility and sustainability perspectives.

The resource utilization efficiency is determined by the ratio of the mass of metal/alloy produced and recycled resources to the total input mass, as defined by the following equation:

$$£ = \frac{(M_p + M_r)}{M_{inp}} \times 100 \quad (3)$$

Where, M_p (Kg) is the mass of the alloy
M_r (Kg) is recycled mass used
M_{inp} (Kg) total input stream mass

The carbon dioxide emission ratio is quantified as the quantity of carbon dioxide (Kg) emitted per metric ton of alloy produced, as defined by the following equation:

$$\mu = \frac{M_{CO_2}}{M_{alloy}} \quad (4)$$

where, M_{CO_2}(Kg) is the mass of CO_2 and CO emitted.
M_{alloy} (Kg) is the mass of alloy generated.

The above two parameters are obtained from the FactSage simulation results.

RESULTS AND DISCUSSION

Thermodynamic analysis of the secondary Cu smelting process

In the first stage, thermodynamic optimization has been done to identify an optimized coal air ratio (CAR) for maximum base metal (copper) recovery and minimum solid carbon residue formation in the output streams. **Figure 1** shows the variation of the optimized coal-air ratio for the maximum recovery of base metal and minimum formation of solid carbon residue in the output streams with the WPCB % in the input stream. CAR variation with WPCB shows that the coal-air ratio value decreases as the percentage of WPCB increases in the input stream. It depicts the requirement for less amount of coal while increasing the WPCB in the Cu smelter for processing. This is attributed to the presence of carbon in the WPCB. The maximum value is 0.875, which is for 0 % E-waste because there will be no plastics. The minimum value is 0.1375, which is for 100 % WPCB because it will have the highest number of plastics.

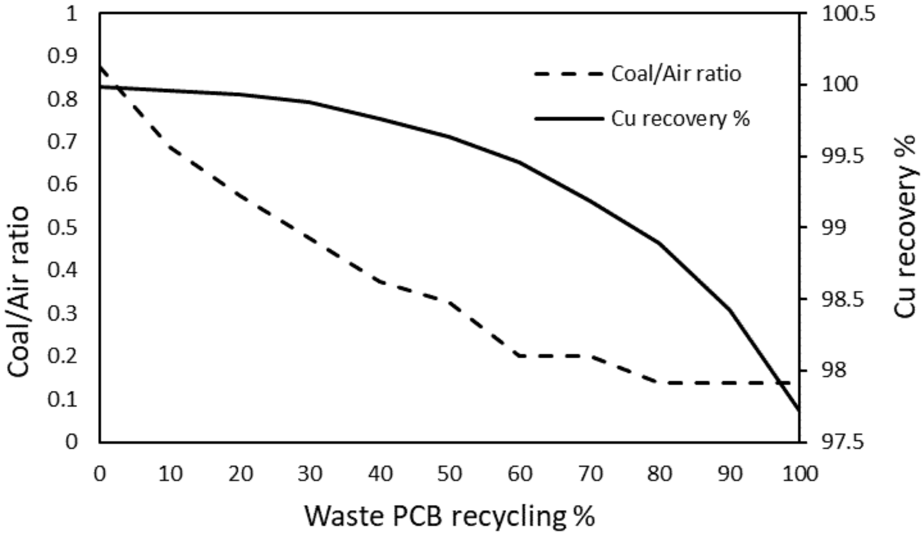

Fig 1: Variation of optimized CAR for different WPCB recycling %

In the second stage of thermodynamic optimization, the optimum process temperature towards the formation of maximum liquid slag along with maximum base metal recovery has been identified. The optimized process temperature was determined considering the CAR in the simulation optimized in the previous step. The temperature in the simulation studies has been varied from 1100 to 1600 °C to identify the optimum process temperature.

In the final stage, an additional parameter i.e., flux (lime) addition, was introduced to facilitate liquid slag and minimize solid slag formation. Optimization of flux addition has been performed to identify the process window for complete liquid slag formation with less viscosity. Introducing lime into the input stream, the intention is to promote the formation of a complete liquid slag with less viscosity. This can significantly improve the overall process performance in terms of refining as well as slag-metal separation. Reducing slag viscosity can facilitate better mass transport, enhancing metal recovery and process efficiency. The simulation experiments have been performed for the optimized CAR and process temperature conditions. Based on the optimization results, the composition of the slag was identified for each case and is presented in **Table 2**, along with the optimized process temperature and viscosity of the slag. Slag viscosity has been estimated using the viscosity module of FactSage 8.1.

Table 2 Optimum CAR, process temperature, slag composition, and viscosity of slag for WPCB recycling in secondary Cu smelter.

WPCB Recycling	**CAR**	**Temperature**	**Al_2O_3**	**SiO_2**	**CaO**	**MgO**	**FeO**	**Viscosity**
(%)	**-**	**(°C)**	**(Wt%)**					**(PaS)**
0	0.875	1350	4.73	61.65	27.58	0	5.21	7.723
10	0.687	1550	26.36	34	36.90	1.96	0.008	0.502
20	0.575	1600	40.72	24.48	32.69	1.59	0.001	0.483
30	0.455	1550	38.74	26.53	32.48	1.96	0.001	0.705
40	0.375	1400	19.91	36.45	40.55	2.96	0.008	0.91
50	0.325	1400	21.24	37.09	38.752	2.84	0.008	1.133
60	0.2	1450	24.17	36.40	36.681	2.69	0.005	0.996
70	0.2	1450	23.64	36.30	37.23	2.76	0.005	0.926
80	0.137	1450	22.39	35.69	38.963	2.915	0.004	0.877
90	0.137	1450	23.835	36.647	36.749	2.745	0.004	0.984
100	0.137	1450	23.51	36.548	37.125	2.784	0.003	0.937

Figure 2 illustrates the variation of copper recovery in the final optimized case as a function of the WPCB recycling percentage. The results indicate a marginal decrease in Cu recovery with an increase in the amount of WPCB in the input stream. The maximum recovery of 99.99%, is observed for the 0% WPCB recycling case, indicating optimal conditions for copper recovery in the absence of WPCB. The initial decrease in the Cu recovery is due to more Cu metal dust formation at higher process temperatures (say 1550 to 1600 °C). When considering the input stream containing WPCB, the maximum copper recovery achieved is 99.93% for the 40% WPCB recycling case. Conversely, the minimum recovery of 99.7% is recorded for the 100% waste recycling case. The content of Cu in the base metal decreases with the WPCB amount in the input stream. Further, the amount of Cu reported to the dust portion increases with WPCB recycling. This may be due to the influence of other elements that join base metals, such as Fe, Sn, and Si, decreasing the activity coefficient of Cu. Considering all these, the 40% WPCB recycling case emerges as the most favorable scenario for achieving maximum copper recovery while recycling WPCB through the secondary copper smelting process.

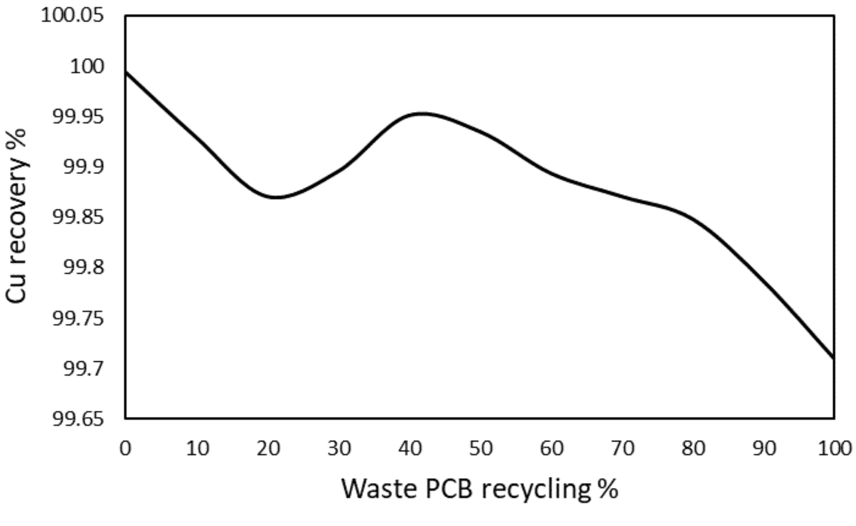

Fig 2: Recovery of Cu during WPCB recycling through secondary Cu smelting under optimized condition

The present work aims to recover the maximum precious metals in black copper along with other base metals such as Fe, Si, Sn, etc. The discussion pertaining to the formation of fume due to high vapor pressure elements present in the scrap and e-waste in relation with the slag formation will be reported as a part of the future work.

Sustainability analysis

The findings of the environmental analysis are presented and discussed in the following sections. **Figure 3(a)** depicts the relationship between resource utilization efficiency and WPCB recycling percentage. The findings demonstrate a clear trend: resource utilization efficiency initially rises with increasing WPCB in the input stream till 30% WPCB recycling case. Subsequently, it declines at 40%, gradually increasing till 100% WPCB recycling scenario. Notably, the minimum resource utilization efficiency is observed when there is no recycling of WPCB (0% recycling case), as it utilizes the least amount of recycled mass in the input stream. Conversely, the maximum resource utilization efficiency occurs at the 100% WPCB recycling case, which utilizes the most recycled mass available.

Figure **3(b)** illustrates the relationship between the carbon emission ratio and WPCB recycling percentage. A similar trend has been observed in resource utilization efficiency. The lowest carbon emission rate is observed when no WPCB is in the input stream. When comparing the cases with WPCB in the input stream, the minimum carbon emission rate occurs at the 40% WPCB recycling case, while the maximum is observed at the 100% WPCB recycling case. This indicates that adopting a recycling rate of 40% WPCB through the secondary Cu smelting process significantly improves the overall environmental and economic sustainability of the process.

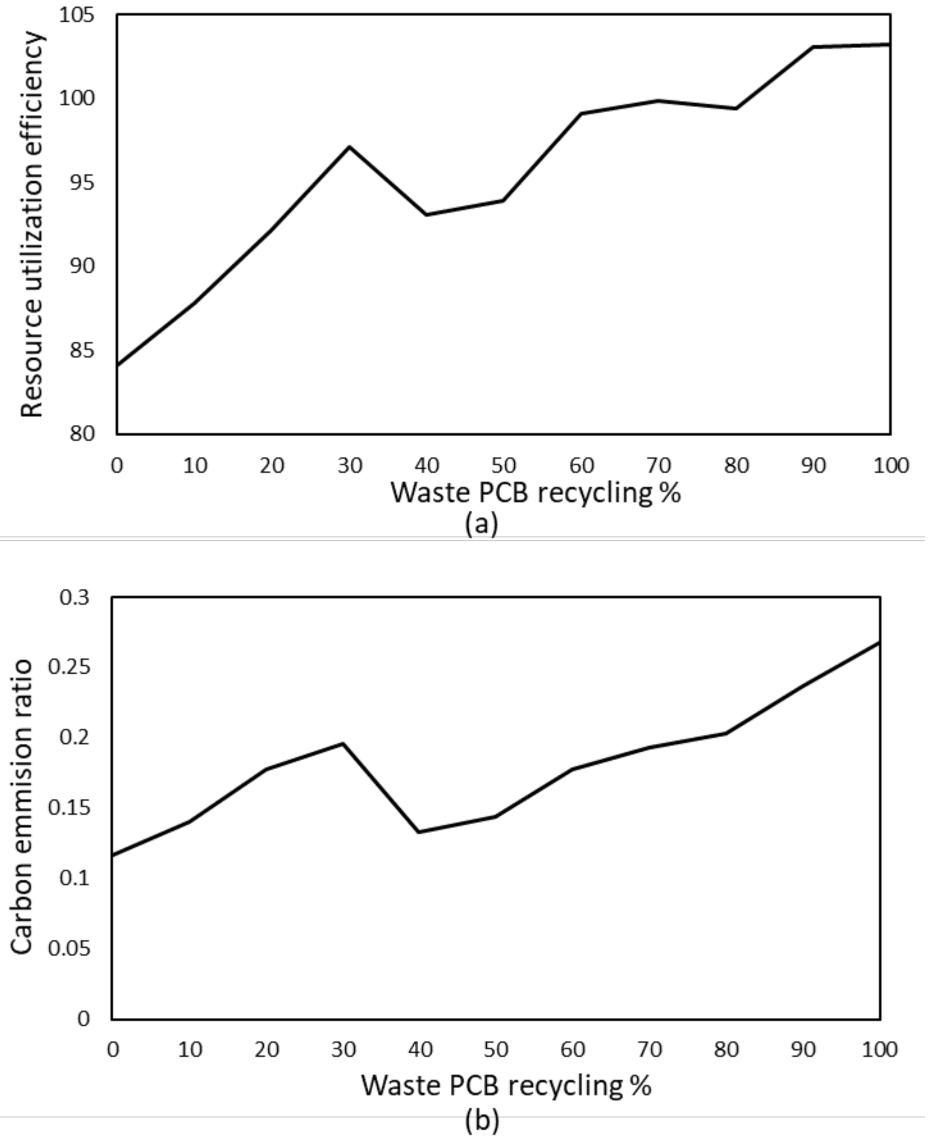

Fig 3: Sustainability assessment of WPCB recycling through secondary Cu smelting route: (a) resource utilization efficiency (b) CO_2 emission rate

CONCLUSIONS

The salient features of the present investigation are as follows,

- The coal-air ratio decreases with an increase in the WPCB in the input stream. This is attributed to the energy demand required for the process being met from the carbon present in WPCB as plastics.
- The minimum process temperature required to form the maximum amount of liquid slag has been identified for different WPCB recycling rates for the optimized CAR. The optimized process temperature varies from 1350 to 1600 °C with extra flux (i.e., lime) addition to form 100% liquid slag for efficient molten metal-slag separation. However operating at such a high temperature will impact the furnace design and metal and slag containment.
- The 40% WPCB recycling through the secondary copper smelting process under the optimized condition emerges as the efficient scenario for achieving maximum base metal recovery, i.e., copper.
- It is observed that the resource utilization efficiency increases with an increase in the WPCB content in the input stream of the process. However, the carbon emission ratio is observed to be minimum (0.133) for 40% of waste PCB recycling cases.

- Adopting a recycling rate of 40% WPCB through the secondary Cu smelting process significantly improves the overall environmental and economic sustainability of the process.

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Annexure

The composition of input streams used in the simulation is given below

a) Cu scrap

Cu	**Cu2O**	**SnO2**	**PbO**	**ZnO**	**NiO**
			(wt%)		
70	7	5	8	5	5

b) E-waste

E-Waste	**Element or compound**	**Wt %**
Metal	Cu	18.36
	Pb	5.50
	Fe	7.98
	Zn	3.67
	Au	0.091
	Ag	0.18
	Al	4.59
	Sn	3.67
	Ni	1.83
Oxide	Al2O3	5.50
	SiO2	22.03
Plastics	C2H3Cl	1.10
	C2H4	2.19
	CH3NO2	0.66
	C7H8O2	1.53
	C12H6Cl4	0.66
	C12H8Br2	2.63
	C15H16O2	13.16
	H2O	4.59

c) Metallurgical coke

C	H2O	S	Al2O3	FeO
90	5	0.8	2	2.2

d) FCS slag

FeO	CaO	SiO2
45	17	38

e) FCS slag

O_2	N_2
54	46

f) Lime

CaO	MgO	SiO2
84.32	6.48	9.18

The composition of black copper produced

Waste PCB recycling (%)	Black copper (Wt%)											
	Ag	Al	Au	Cu	Fe	Mg	Ni	Pb	Si	Sn	Zn	Ag
0	0.00	0.00	0.00	81.85	1.23	0.00	4.22	6.87	0.00	4.23	1.60	0.00
10	0.02	0.06	0.01	82.46	2.38	0.00	4.36	4.63	1.02	4.58	0.47	0.02
20	0.04	0.38	0.02	80.86	3.54	0.00	4.40	3.04	2.60	4.87	0.24	0.04
30	0.07	0.35	0.04	78.43	4.83	0.00	4.40	2.99	3.49	5.15	0.23	0.07
40	0.10	0.02	0.05	76.20	6.34	0.00	4.44	5.94	0.64	5.51	0.75	0.10
50	0.14	0.02	0.07	74.05	8.17	0.00	4.52	5.46	0.97	5.97	0.63	0.14
60	0.18	0.06	0.09	71.59	10.38	0.00	4.62	3.64	2.56	6.54	0.33	0.18
70	0.23	0.06	0.12	68.33	13.04	0.00	4.72	3.08	2.91	7.20	0.28	0.23
80	0.29	0.07	0.15	64.31	16.37	0.00	4.86	2.57	3.09	8.04	0.24	0.29
90	0.36	0.06	0.20	58.68	20.47	0.00	4.99	1.79	4.23	9.02	0.18	0.36
100	0.43	0.06	0.25	51.49	25.89	0.00	5.17	1.19	5.00	10.33	0.13	0.43