Modeling, simulation and technical assessment of spent Li-ion batteries recycling plant

Á. Imre-Lucaci, A.-M. Cormoş*, F. Imre-Lucaci** and Sz. Fogarasi**

**Department of of Chemical Engineering, Faculty of Chemistry and Chemical Engineering,*
Babeş-Bolyai University, Cluj-Napoca, RO-400028, Romania

***Institute for Interdisciplinary Research in Bio-Nano-Sciences, Babeş-Bolyai University, Cluj Napoca,*
RO-400271, Romania

Presenting author e-mail: szabolcs.fogarasi@ubbcluj.ro

Introduction

Based on the current tendency it is estimated that on global scale the LIBs industry will reach in 2026 the capacity of 1000 GWh corresponding to almost USD 140 billion which is almost four times the value reported in 2019 and only half of the capacity predicted for 2030 [1, 2]. It is undeniable that LIB production is on an ascendant trajectory, increasing from year to year in correlation with other industrial sectors, which boosts energy and raw material consumption to a level that clearly cannot be economically sustained by current supplies without a proper recycling [2]. Besides the deepening gap between demand and supply, generated by the increase of raw materials uncertainty and unavailability, there is a new challenge on the horizon associated with the accumulation of an estimated 300 million ton of spent LIB (SLIB) in the next 20 years [3].

Despite the large number of novel recycling approaches published recently the majorities of studies are performed only at laboratory level and deal with the processing of different material fractions from SLIB without offering an overall solution that can be deployed for industrial application.

The current study comes to close this gap by providing a quantitative assessment of various process concepts designed for the treatment of the complete SLIB. Process flow modeling software was used to evaluate the contribution of all process steps and equipment to the overall energy consumption and to the mass balance data required for the technical assessment of the large-scale recycling plant. To underline the advantages and identify the optimal novel process concept several key performance indicators were determined such as recovery efficiency, specific energy/material consumptions, specific CO_2 emissions, etc.

Results and Discussion

The process is divided into the following subsystems (the PFD developed in CHEMCAD is presented in Fig. 1):

1 - The mechano-thermal treatment of LIBs
2 - Dissolution and purification
3 - Separation and recovery of manganese
4 - Dissolution of magnetic metals
5 - Separation and recovery of cobalt
6 - Separation and recovery of nickel
7 - Separation and recovery of lithium.

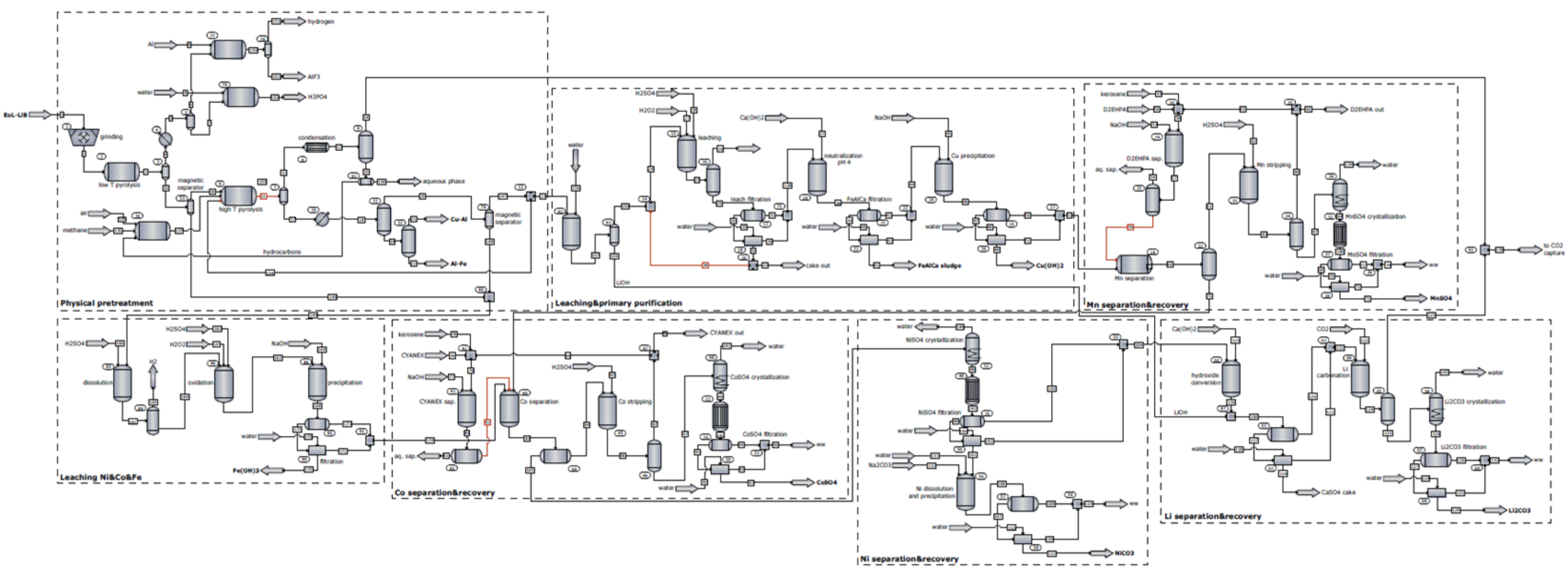

Fig. 1. Process flow diagram of the spent Li-ion batteries recycling plant.

The evaluation of the technical performances for the recovery processes of metals from spent LIBs based on the defined mathematical models were carried out by simulating and optimizing the processes using process flow modeling software CHEMCAD specific to chemical engineering.

In order to identify the optimal systems for metal recovery from spent LIBs, the technical performances of the thermally integrated/non-integrated technological variants, respectively with and without CO_2 capture, were compared. In addition, the impact of the type of reducing agent (H_2O_2, $C_6H_8O_7$, HCOOH and $H_2C_2O_4$) on the performance of the spent LIBs recycling plant was assessed.

For the evaluation of the technical performances of the process the following cases were considered:

- **Case I** - thermally non-integrated process - to generate the thermal energy requirement, combustion of additional amounts of CH_4 was considered
- **Case II** - thermally integrated process - with H_2 combustion
- **Case III** - integrated thermal process with recirculation of CO_2 and water into the process.

Table 1. Recovery yields (in %) and production rates (in kg/h) for the main products of the spent LIB recycling process.

Product	$MnSO_4{\cdot}H_2O$	$CoSO_4{\cdot}7H_2O$	$NiCO_3$	Li_2CO_3	$Fe(OH)_3$	Graphite	Al	Cu
Production rate	206.63	299.03	208.76	131.81	98.77	189.71	296.25	101.5
Recovery yield	84.09	79.26	82.61	94.84	98.21	87.50	93.24	90.91

Table 2. Specific consumption of raw materials in kg/kg LIB for the spent LIB recycling process.

Raw material	H_2O	CH_4	H_2SO_4	Na_2CO_3	NaOH	air	$Ca(OH)_2$	CO_2	TOTAL
Consumption	2544	120	1019.7	211.98	424.76	3500	137	98.5	-
I	1.94	0.09	0.78	0.16	0.32	11.39	0.10	0.07	14.85
II	1.94	0.09	0.78	0.16	0.32	2.66	0.10	0.07	6.17
III	1.10	0.09	0.78	0.16	0.32	2.66	0.10	0	5.22

Table 3. Specific consumption of raw materials in kg/kg product for different subsystems of the spent LIB recycling process using oxalic acid.

Subsystem	1	2	3	4	5	6	7
TOTAL, kg/h	4959.5	801.86	727.10	1145.69	693.60	861.98	272.50
W, kg/kg	3.77	2.08	3.52	4.61	2.32	4.13	2.07

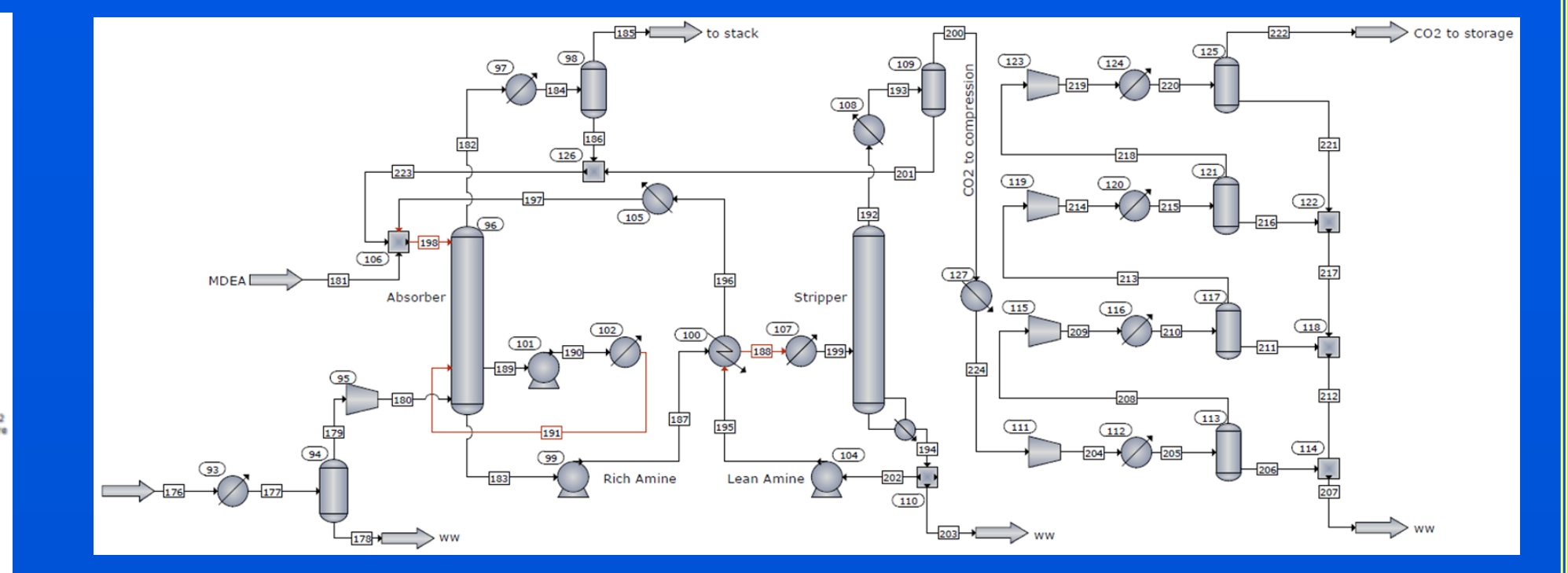

Fig. 2. PFD for the CO_2 capture process.

Considering the importance of CO_2 capture in the industrial sector, the recycling plant of spent LIBs was coupled with a post-combustion CO_2 capture based on amine absorption process (the PFD developed in CHEMCAD is presented in Fig. 2).

Table 4. Thermal energy balance for the spent LIB recycling process using oxalic acid.

Subsystem	Parameters of energy flows	Thermal energy generated			Thermal energy consumed			TOTAL consumption, MJ/h	Specific consumption, MJ/kg	Equivalent consumption, kg CH_4/h
		1	2	3	1	2	3			
1	T, °C	120	40	380	370	797				
	Q, MJ/h	-488	-51	-11269	1173	76		1249	0.95	25
2	T, °C	60								
	Q, MJ/h	-1704						0	0	0
3	T, °C	24			24	40	25			
	Q, MJ/h	-1687			1469	271	419	2159	10.45	43
4	T, °C	32			40					
	Q, MJ/h	-1713			700			700	2.82	14
5	T, °C	24			24	40	25			
	Q, MJ/h	-1395			1384	5057	582	7023	23.49	140
6	T, °C	40	110		110					
	Q, MJ/h	-258	-583		2129			2129	10.20	43
7	T, °C	35			93					
	Q, MJ/h	-112			387			387	2.94	8
I								13646		273
II	T, °C	380			370	797				
	Q, MJ/h	-3781			1173	76		1249	0.95	25

Table 5. Total and specific CO_2 emissions, respectivelly the average energy consumption of the CO_2 capture process for the recycling of spent LIBs.

Process type	I		II		II with H_2 combustion		II with H_2 combustion and partial reuse of CO_2 in the process	
Reducing agent	Total, kgCO_2/h	kg CO_2/kg LIB	Total, kgCO_2/h	kg CO_2/kg LIB	Total, kgCO_2/h	kg CO_2/kg LIB	Total, kgCO_2/h	kg CO_2/kg LIB
H_2O_2	1402	1.07	652	0.50	516	0.39	417	0.32
$C_6H_8O_7$	1418	1.08	667	0.51	517	0.39	418	0.32
HCOOH	1425	1.08	675	0.51	525	0.40	426	0.32
$H_2C_2O_4$	1449	1.10	698	0.53	548	0.42	449	0.34
CO_2 capture energy consumption, GJ/h	4.73		2.24		1.75		1.42	

Conclusions

- ► Based on the energy balance data it can be concluded that the process remains a thermal energy generator even with CO_2 capture, producing 1.5 GJ/h for thermally integrated process, ~2 GJ/h for thermally integrated process with H_2 combustion and 2.3 GJ/h for thermally integrated process with H_2 combustion and partial reuse of CO_2
- ► As an overall conclusion it can be stated that the technological option with H_2 combustion and partial reuse of CO_2 is the most efficient in terms of recycling spent LIBs regardless of the reducer used.

References

1. Miao, Y., Liu, L., Xu, K., Li, J., 2023. *High concentration from resources to market heightens risk for power lithium-ion battery supply chains globally*. Environ Sci Pollut Res Int 30, 65558-65571.
2. Shi, G., Cheng, J., Wang, J., Zhang, S., Shao, X., Chen, X., Li, X., Xin, B., 2023. *A comprehensive review of full recycling and utilization of cathode and anode as well as electrolyte from spent lithium-ion batteries*. Journal of Energy Storage 72, 108486.
3. Thompson, D., Hyde, C., Hartley, J.M., Abbott, A.P., Anderson, P.A., Harper, G.D.J., 2021. *To shred or not to shred: A comparative techno-economic assessment of lithium ion battery hydrometallurgical recycling retaining value and improving circularity in LIB supply chains*. Resources, Conservation and Recycling 175, 105741.

Acknowledgements

This work was supported by a grant of the Ministry of Research, Innovation and Digitization of the Romanian Government, CNCS/CCCDI - UEFISCDI, project code COFUND-LEAP-RE-RESTART, within PNCDI III.

This project has received funding from the European Union's Horizon 2020 Research and Innovation Program under Grant Agreement 963530.