LIFE CYCLE INVENTORY OF OIL SHALE RETORTING BY-PRODUCTS FOR PRODUCTION OF RESINS

GUSCA J.[1], SIIRDE A.[1] and ELDERMANN M.[1]

[1] Department of Thermal Engineering, Tallinn University of Technologies, Ehitajate tee 5, 19086, Tallinn, Estonia
E-mail: julija.gusca@ttu.ee

ABSTRACT

High reactive alkyl derivatives of resorcinol, the main component of total phenols, are significant raw material for production of synthetic tanning agents, various adhesive resins and plugging compositions for insulation materials. Traditionally resins production relates to high resources consuming industry, therefore additional attention needs to be paid for reduction of environmental pollution from it. Use of by-products is considered as a good waste minimization and resource consumption reduction tool that brings in addition financial benefits to industry.

A life cycle inventory (LCI) study of resins production from retort liquor extracted from Estonian oil shale is presented in the paper and it follows the requirements of ISO 14040 and 14044 standarts. The goal of the study is to define the life cycle inventory indicators for identification of the improvement potential of environmental impacts of resins production from oil shale retorting by-products. Data inventory and boundaries of the modelled system corresponds to the oil shale processing plant of the Viru Keemia Grupp Oil AS (VKG) located in Kohtla Järve, Estonia. Technological boundary of the system is starting from treatment of raw materials and ending with production of resins; transportation to market, use of resins for further production chains and end of life phase are excluded from the system. Time boundary of the inventory data corresponds to the year 2013.

The findings of the LCI based environmental analysis shows that the dephenolation unit has the greatest cumulative environmental impact in the categories “Energy use” and “Water use”, followed by the “Treatment of pure phenolics unit”, the “Synthesis unit” and the less harmful “Phenols distillation unit”. However, the phenols distillation process generates the most of the emissions to air. On the basis of the performed life cycle inventory, a life cycle assessment will follow.

Keywords: oil shale, phenol-formaldehyde resol resins, by-products, life cycle inventory indicators, ranking.

1. Introduction

Environmental policy initiatives regularly stimulate industrial companies to work on minimisation of environmental impacts and optimisation of industrial processes. Chemical processes are considered as one of the energy and material intensive that put the effect to the environmental performance of the industry (Negny *et al*. 2012). Several studies (Choi *et al*. 2015; Hischier *et al*. 2005; Klöpffer 2005; Kobayashi 2006; McDevitt and Grigsby 2014; La Rosa *et al*. 2014; Silva *et al*. 2014) have introduced life cycle analysis framework to evaluate the environmental performance of resins production with a special focus mainly evaluating the possibilities to produce those from biobased materials. At the same time the environmental impacts of resins production from oil shale processing by-products, thus eliminating amount of emissions and wastes released to the environment, were not analysed yet. Thermal processing and retorting of oil shale for extraction of liquid fuel results to formation of significant amount of processing water and wastewaters containing phenols, tars and other toxic substances harmful for the environment (Kamenev *et al*. 2003). In addition, high content alkyl resorcinols is typical for the oil shale processing water outflows (Kekisheva *et al*. 2007).

This paper describes a Life Cycle Inventory (LCI) of relevant inputs and outputs and the associated emissions to air from the phenol-formaldehyde resol resins production from oil shale processing by-product. The primary objective of the paper is to define the life cycle inventory indicators for identification of the improvement potential of environmental impacts in three impact categories – emissions to air, energy and water use. The current study is a part of an integrated assessment of the motor fuel production from oil shale industry.

2. Materials and methods

A Life Cycle Inventory (LCI) is the first step to assess a product's life-cycle environmental performance using the Life Cycle Assessment methodological framework. The study includes two components: (1) definition of the goal and scope, system's boundaries and functional unit and (2) the inventory of material and energy inputs and outputs throughout the life-cycle of resins production within the oil shale processing industry. The main goal of the study is to define the resource and energy requirements and the direct emissions to air generated in the production process of the phenol-formaldehyde resol resins from oil shale processing industry related by-product – phenolic water. The quantitative indicators of LCI processes also indicate a benchmark for environmental improvements.

To perform an accurate comparison of the results as well as to calculate in an appropriate way the input and output flows of the system, a functional unit (FU) is defined. There are at least seven types of phenol based resins produced within the analysed system. However, to maximise the impact and use of the gained results, the final product was generalised to phenol-formaldehyde resol resins. Thus the selected FU is 1 kg of the phenol-formaldehyde resol resins produced and all energy, mass and emissions balances relate to the 1 FU. Mass allocation approach is selected for the study.

System boundary illustrates the processes included under the evaluation system. The system boundaries defined for the present study are shown in Fig. 1. A cradle-to-gate approach is selected for the study, starting from treatment of raw materials and ending with production of resins; transportation to market, use of resins for further production chains and end of life phase are excluded from the system. As shown in Fig. 1, the evaluated system is divided in 4 subsystems: dephenolation unit, distillation of phenols distillation unit, treatment of pure phenols and synthesis unit. Construction and decommissioning phases are not included in the study as it is observed that the impacts of these phases might be comparative with the traditional phenol-formaldehyde resol resin production system, thus might be excluded from the assessment.

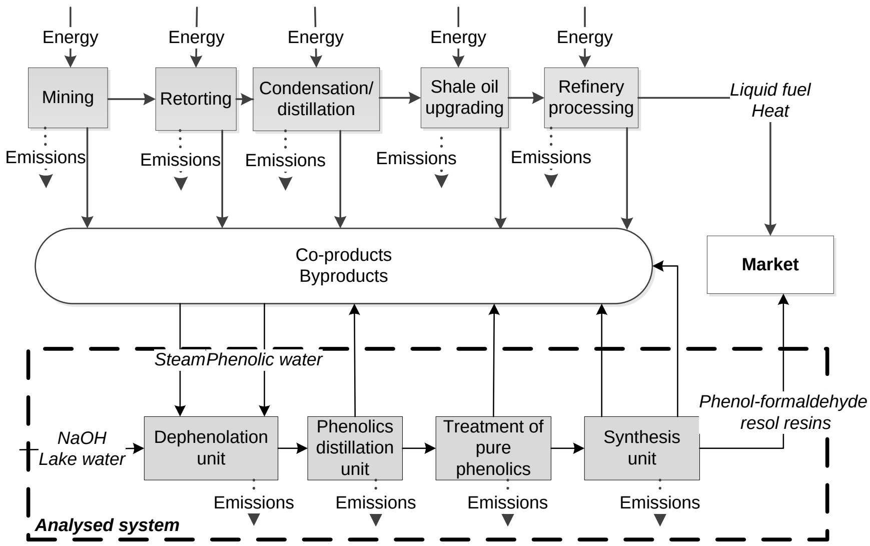

Figure 1: Life cycle flowchart of the resorcinols production.

The dephenolation unit includes extraction of light organic compounds from phenol water, additional distillation of total phenols with extracting agent (5-10% extracting agent). In the distillation of phenols unit the total phenols exiting the dephenolation unit are processed to extracting agent, 2 MR fraction and other phenolic fractions as finished products and raw material for synthesis of resins get honeyol and rezol. Phenolic distillation residues generated in the phenolic distillation unit are used later in the oil distillation unit as raw materials for production of relevant chemicals. In the next subsystem (treatment of pure phenols), the distillated fractions of phenols are rectificated and fed further to the synthesis unit for the final treatment. There, during crystallization phase, the pure phenol products are produced- 2MR, 5MR anhydride and 5MR monohydride. Residues of the synthesis unit are delivered to the distillation of phenols unit for further recycling and recovery.

3. Results

The energy and mass balances of the phenol-formaldehyde resol resins production analysed within the study are gathered from the following sources: data collected from the case plant (reports, measurements, monitoring data), interviews with experts at the case plant, calculations, research reports and papers, LCI databases incorporated in the SimaPro 8 software (mainly Ecoinvent v2.2. database was explored). In addition, the following assumptions were introduced in the study: (1) industry energy and material flow data used in the LCI is annual levelirised data; (2) taking into account the commercial responsibility issues of the VKG plant, a mass based allocation method were selected in the study to assign the environmental burdens of the phenol-formaldehyde resol resins within the system boundary.

Table 1: The LCI of the phenol-formaldehyde resol resins production.

	Value	Unit	Data source quality
Inputs			
Phenolic water	1.03	1000 m^3	Good - industry and calculation data
NaOH for pH regulation	0.03	tonne	Good - calculation
Lake water	0.11	m^3	High - industry data
Circulating cooling water	3.68	1000 m^3	Good - industry and calculation data
Energy			
Electricity	3.16	MWh	High - industry data
Steam	126.32	MWh	Good - industry and calculation data
Heating gas	0.87	tonne C	High - industry data
By-products			
Dephenolated water	1.17	1000 m^3	Good - calculations
Residues to oil distillation unit	0.06	tonne	Good - industry and calculation data
Crystallisation cube residues	0.05	tonne	Good - industry and calculation data
Air emissions			
NO_2	1541.58	gramms	Good – calculation and monitoring data
CO	1.54	gramms	
VOC	0.10	gramms	
CO_2	1406.65	gramms	
phenol	0.04	gramms	
butyl acetate	0.55	gramms	
formaldehyde	0.02	gramms	
methanol	0.03	gramms	
toluene	0.04	gramms	

As stated before, the phenol-formaldehyde resol resins are produced from the phenolic water – a by-product of the oil shale thermal processing to liquid fuel. The phenolic water consists of various compounds (e.g. mono- and dibasic phenols, carboxylic acids, ketones, basic nitrogen compounds, etc.) (Kekisheva *et al*. 2007). The phenolic water yield depends on the retorting process of the oil shale: for example, it was experimentally defined that total yield of phenols from the Kiviter retorting semicoking water is 140 kg per tonne of processed oil shale (Kamenev *et al*. 2003) (see the data in Table 1).

Electricity used in the chemical processes is taken from the VKG combined heat and electricity plant: oil shale derived generator gas is used as a fuel there. Steam from the resins productions is delivered from the retorting system, where it is used for thermal processing of oil shale rocks. Due to the reason that transportation of steam is internal process, and the distance does not exceed 2 kilometres, the transportation of steam is excluded from the study. Circulating water is used only for cooling needs and the time of use exceeds 1 year, thus a minimal amount of compensation water is required and the lake water is used for these needs. Performing the quantitative analysis of the LCI indicators (see Table 1), a ranking table of the impact categories was developed (see Table 2).

Table 2: Ranking of the impact categories of the resol resins production.

Category	Dephenolation	Phenols distillation	Pure phenolic production	Synthesis
Energy use	1	4	2	3
Water use	1	3	4	2
Emissions to air	2	1	4	3

As shown, the dephenolation unit gives the most significant impacts to the environment in the resource consumption categories, while phenols distillation generates the highest emissions to air.

4. Conclusions

The Life Cycle Inventory (LCI) of the phenol-formaldehyde resol resins production from oil shale processing by-product – phenolic water presented in this study has been used to define the categories potential for the minimisations of environmental impacts. The LCI based indicators show that additional efforts need to be focused to optimise the energy and water use in the dephenolation unit and emissions in the phenols distillation processes. The follow-on Life Cycle Assessment gives a platform for comparison of the environmental profile of the modelled production process with other resins production technologies and identification of the significant parameters through sensitivity analysis.

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