Supplementary Information

What to do with Polyurethane waste? - The environmental potential of chemically recycling Polyurethane rigid foam

Martin Pillich[a], Johannes Schilling[a], Luca Bosetti[a], André Bardow[a]

[a] Energy & Process Systems Engineering, ETH Zurich, Zurich, Switzerland

Corresponding author

Prof. Dr.-Ing. André Bardow

Energy & Process Systems Engineering

ETH Zürich

Tannenstrasse 3

8092 Zürich

E-Mail: abardow@ethz.ch

Content

S1 Calculating the composition of PUR rigid foam

Table S1: Considered ratio of precursor for production of PUR rigid foam according to patent from Covestro.[1]

Precursor	weight-%
Polyol with hydroxyl number 450	30.1
Polyol with hydroxyl number 400	8.6
Polyol with hydroxyl number 112	2.58
Catalyst	0.86
Stabilizer	0.86
Isocyanate	57

We calculate the amount of polyol and isocyanate required for the PUR rigid foam analyzed in this study based on the precursor compositions in Table S1. We group all polyol precursors into one type of polyol (PPG-400), assume one type of Isocyanate (MDI) and neglect the catalyst and stabilizer in the overall composition. Those assumptions lead to the following compositions for 1kg of PUR rigid foam:

$$\text{Polyol: } m_{\text{Polyol}} = \frac{(301+86+25.8)\text{g}_{\text{Polyol}}}{(301+86+25.8+570)\text{kg}_{\text{PUR}}} = 420\,\frac{\text{g}_{\text{Polyol}}}{\text{kg}_{\text{PUR}}}$$

$$\text{Isocyanate: } m_{\text{Isocyanate}} = \frac{570\text{g}_{\text{MDI}}}{(301+86+25.8+570)\text{kg}_{\text{PUR}}} = 580\,\frac{\text{g}_{\text{MDI}}}{\text{kg}_{\text{PUR}}}$$

S2 Calculating mass flows of recycling products

We calculate the mass flows of the recycling products according to the composition calculated in Section S1 and the molecular structure:

$$\text{MDA: } m_{\text{MDA}} = 580\,\frac{\text{g}_{\text{MDI}}}{\text{kg}_{\text{PUR}}} * \frac{1}{250.25}\,\frac{\text{mol}_{\text{MDI}}}{\text{g}_{\text{MDI}}} * 1\,\frac{\text{mol}_{\text{MDA}}}{\text{mol}_{\text{MDI}}} * 198.27\,\frac{\text{g}_{\text{MDA}}}{\text{mol}_{\text{MDA}}} = 460\,\frac{\text{g}_{\text{MDA}}}{\text{kg}_{\text{PUR}}}$$

$$\text{Aniline: } m_{\text{aniline}} = 460\,\frac{\text{g}_{\text{MDA}}}{\text{kg}_{\text{PUR}}} * \frac{1}{198.27}\,\frac{\text{mol}_{\text{MDA}}}{\text{g}_{\text{MDA}}} * 2\,\frac{\text{mol}_{\text{aniline}}}{\text{mol}_{\text{MDA}}} * 93.13\,\frac{\text{g}_{\text{aniline}}}{\text{mol}_{\text{aniline}}} = 431\,\frac{\text{g}_{\text{aniline}}}{\text{kg}_{\text{PUR}}}$$

$$\text{Benzene: } m_{\text{benzene}} = 431\,\frac{\text{g}_{\text{aniline}}}{\text{kg}_{\text{PUR}}} * \frac{1}{93.13}\,\frac{\text{mol}_{\text{aniline}}}{\text{g}_{\text{aniline}}} * 1\,\frac{\text{mol}_{\text{benzene}}}{\text{mol}_{\text{aniline}}} * 78.1\,\frac{\text{g}_{\text{benzene}}}{\text{mol}_{\text{benzene}}} = 363\,\frac{\text{g}_{\text{benzene}}}{\text{kg}_{\text{PUR}}}$$

S3 Calculating mass flows and composition of residuals

We calculate the mass flows and the composition of the residuals based on elemental mass balances for carbon (C), hydrogen (H), nitrogen (N), and oxygen (O):

$$m_{i,\mathrm{Residuals}} = m_{i,\mathrm{PUR}} - m_{i,\mathrm{RecyclingProduct}} \ \forall\ i \in [\mathrm{C},\mathrm{H},\mathrm{N},\mathrm{O}]$$

$$m_{\mathrm{total,Resdiuals}} = \sum_i m_{i,\mathrm{Residuals},}$$

Table S2 shows the resulting elemental composition and total mass flows for the residual waste per recycling option.

Table S2: Residual mass flows and composition per kg PUR treated with the respective recycling option

Option	m_C	m_H	m_N	m_O	$m_\mathrm{total} = \sum m_i$
1. Residuals of MDI + Polyol	0g	0g	0g	0g	0g
2. Residuals of Polyol	414g	25g	62g	78g	580g
3. Residuals of MDI	245g	45g	0g	130g	420g
4. Residuals of MDA	301g	35g	0g	204g	540g
5. Residuals of aniline	330g	35g	0g	204g	569g
6. Residuals of benzene	330g	41g	62g	204g	637g
7. Residuals of patent mixture	398g	44g	14g	204g	660g

The elemental masses $m_{i,\mathrm{PUR}}$ are based on the composition of the PUR rigid foam calculated in Section S1 and the elemental compositions of MDI and polyol. The elemental composition of MDI is given by the chemical formula of MDI which is $C_{15}H_{10}N_2O_2$.

As the polyol, PPG-400, is a mixture of multiple polypropylene glycols (PPG) with varying molecular weight (which average 400 $\frac{\mathrm{g}}{\mathrm{mol}}$ in the mixture), we assume the elemental composition of the polyol based on a mixture of two pure PPGs with 6 respectively 7 repeating units (see molecular structure of polyol in Figure 1): One has a molecular weight of 366.56 $\frac{\mathrm{g}}{\mathrm{mol}}$ and the chemical formula $C_{18}H_{38}O_7$ and the other one has a molecular weight of 424.64 $\frac{\mathrm{g}}{\mathrm{mol}}$ and the chemical formula $C_{21}H_{44}O_8$.

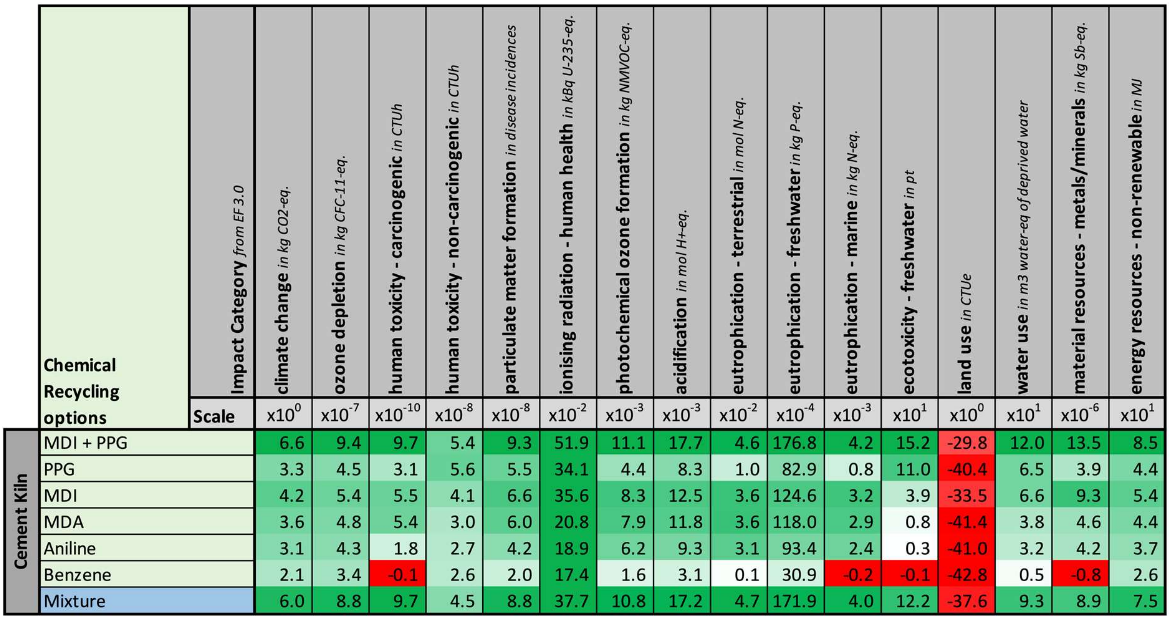
Accordingly, the elemental masses of the recovered recycling products $m_{i,\mathrm{RecyclingProduct}}$ are based on the mass flow calculations in Section S2 and the chemical formulas of MDA ($C_{13}H_{14}N_2$), aniline (C_6H_7N), benzene (C_6H_6) and p-toluidine (C_7H_9N)

S4 Datasets used from LCA databases

Table S3: Sources of LCA datasets used in the study.

process	Location	Source
market group for heat, central or small-scale, natural gas	RER	Ecoinvent 3.8[2]
miscanthus production	DE	
market for lignite	RER	
market group for electricity, medium voltage	RER	
market group for heat, central or small-scale, other than natural gas	RER	
treatment of waste polyurethane, sanitary landfill	RoW	
aniline	EU-27	cm.chemicals v1.01[3]
polypropylene glycol (PPG 400)	EU-27	
benzene	EU-27	
methylene diphenyl diisocyanate	EU-27	
p-toluidine	EU-27	
acetone	EU-27	
4,4'-methylenedianiline	EU-27	

S5 Results for biomass-fired cement kilns



	Chemical Recycling options	**Impact Category** *from EF 3.0*	**climate change** *in kg CO2-eq.*	**ozone depletion** *in kg CFC-11-eq.*	**human toxicity - carcinogenic** *in CTUh*	**human toxicity - non-carcinogenic** *in CTUh*	**particulate matter formation** *in disease incidences*	**ionising radiation - human health** *in kBq U-235-eq.*	**photochemical ozone formation** *in kg NMVOC-eq.*	**acidification** *in mol H+-eq.*	**eutrophication - terrestrial** *in mol N-eq.*	**eutrophication - freshwater** *in kg P-eq.*	**eutrophication - marine** *in kg N-eq.*	**ecotoxicity - freshwater** *in pt*	**land use** *in CTUe*	**water use** *in m3 water-eq of deprived water*	**material resources - metals/minerals** *in kg Sb-eq.*	**energy resources - non-renewable** *in MJ*
		Scale	x10^{0}	x10^{-7}	x10^{-10}	x10^{-8}	x10^{-8}	x10^{-2}	x10^{-3}	x10^{-3}	x10^{-2}	x10^{-4}	x10^{-3}	x10^{1}	x10^{0}	x10^{1}	x10^{-6}	x10^{1}
Cement Kiln	MDI + PPG		6.6	9.4	9.7	5.4	9.3	51.9	11.1	17.7	4.6	176.8	4.2	15.2	-29.8	12.0	13.5	8.5
	PPG		3.3	4.5	3.1	5.6	5.5	34.1	4.4	8.3	1.0	82.9	0.8	11.0	-40.4	6.5	3.9	4.4
	MDI		4.2	5.4	5.5	4.1	6.6	35.6	8.3	12.5	3.6	124.6	3.2	3.9	-33.5	6.6	9.3	5.4
	MDA		3.6	4.8	5.4	3.0	6.0	20.8	7.9	11.8	3.6	118.0	2.9	0.8	-41.4	3.8	4.6	4.4
	Aniline		3.1	4.3	1.8	2.7	4.2	18.9	6.2	9.3	3.1	93.4	2.4	0.3	-41.0	3.2	4.2	3.7
	Benzene		2.1	3.4	-0.1	2.6	2.0	17.4	1.6	3.1	0.1	30.9	-0.2	-0.1	-42.8	0.5	-0.8	2.6
	Mixture		6.0	8.8	9.7	4.5	8.8	37.7	10.8	17.2	4.7	171.9	4.0	12.2	-37.6	9.3	8.9	7.5

Figure S1: Environmental potentials for the 7 recycling options when compared to replacing biomass in cement kilns.

Figure S1 shows the environmental potential of PUR rigid foam recycling when the utilization of PUR rigid foam in cement kilns is considered as the benchmark and miscanthus is replaced instead of lignite.

In this case, PUR rigid foam recycling has positive environmental potentials for almost all impact categories. Compared to the replacement of lignite, all chemical recycling options have positive environmental potentials in the impact category “eutrophication - freshwater”. However, now, a negative potential is identified in the impact category "land use" for all recycling options: as cultivating miscanthus to replace the PUR rigid foam causes high environmental impacts in “land use”, any potential credits from the avoided production of the chemical recycling products are smaller than those cultivation impacts.

Additionally, for the recycling to benzene (option 6), burden shifting occurs for the impact categories “human toxicity - carcinogenic”, “eutrophication – marine”, “ecotoxicity - freshwater” and “material resources – metals/minerals” due to low credits for benzene and high emissions from residual waste treatment, as discussed in the Section 3.1 in the main manuscript.

S6 Calculating the minimum conversion rate

The environmental potential depends on the conversion rate (CR) of the recycling process. A decrease in the conversion rate results in a lower mass of recycling products and hence a higher mass of residuals (see mass balances in Section S3), i.e., $m_{\text{total,RecyclingProduct}}(\text{CR})$ as well as $m_{\text{total,Residuals}}(\text{CR})$.

If the environmental potential for a conversion rate of 100% is positive, a decrease of the conversion rate will decrease this environmental potential. The minimal conversion rate (MCR) is defined as the conversion rate where the environmental potential reaches a value of 0.

$$0 = E_{\text{Pot}}(\text{MCR})$$

$$0 = EI_{\text{WT,net}} - EI_{\text{CR,ideal,net}}(\text{MCR})$$

$$0 = EI_{\text{WT,net}} - \Big(EI_{\text{CR,ideal,direct}}\big(m_{\text{total,Residuals}}(\text{MCR})\big) - EI_{\text{avC}}\big(m_{\text{total,RecyclingProduct}}(\text{MCR})\big)\Big)$$

S7 Changes in heating value of residuals wastes due to lower conversion rates

The amount of energy recovered from the residual waste incineration depends on the mass and the heating value of the residuals waste.

Heating values of the residuals wastes with varying compositions are calculated using the equation of Boie[4]:

$$\mathrm{LHV} = 34.8\frac{MJ}{kg} * \frac{m_{\mathrm{C}}}{m_{\mathrm{total}}} + 93.9\frac{MJ}{kg} * \frac{m_{\mathrm{H}}}{m_{\mathrm{total}}} + 6.3\frac{MJ}{kg} * \frac{m_{\mathrm{N}}}{m_{\mathrm{total}}} - 10.8\frac{MJ}{kg} * \frac{m_{\mathrm{O}}}{m_{\mathrm{total}}}$$

As shown in Section S3, the mass and elemental composition of the residuals waste is determined by the recycling products produced. If the mass of products decreases due to lower conversion rates, the mass of the residual waste increases and the composition changes.

References

1 World Intellectual Property Organization, WO2022253873A1, 2022.

2 G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz and B. Weidema, *Int J Life Cycle Assess*, 2016, **21**, 1218–1230.

3 L. Stellner, A. Kätelhön, O. Vögler, R. Hermanns, S. Sangwon, A. Bardow and R. Meys, *Methodology cm.chemicals Version 1.01*, Carbon Minds GmbH, Cologne, 2022.

4 E. Doering, H. Schedwill and M. Dehli, *Grundlagen der Technischen Thermodynamik*, Springer Fachmedien, Wiesbaden, 2016.