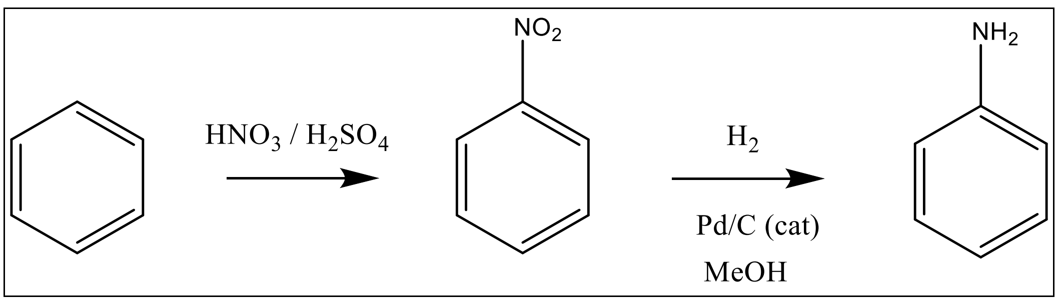
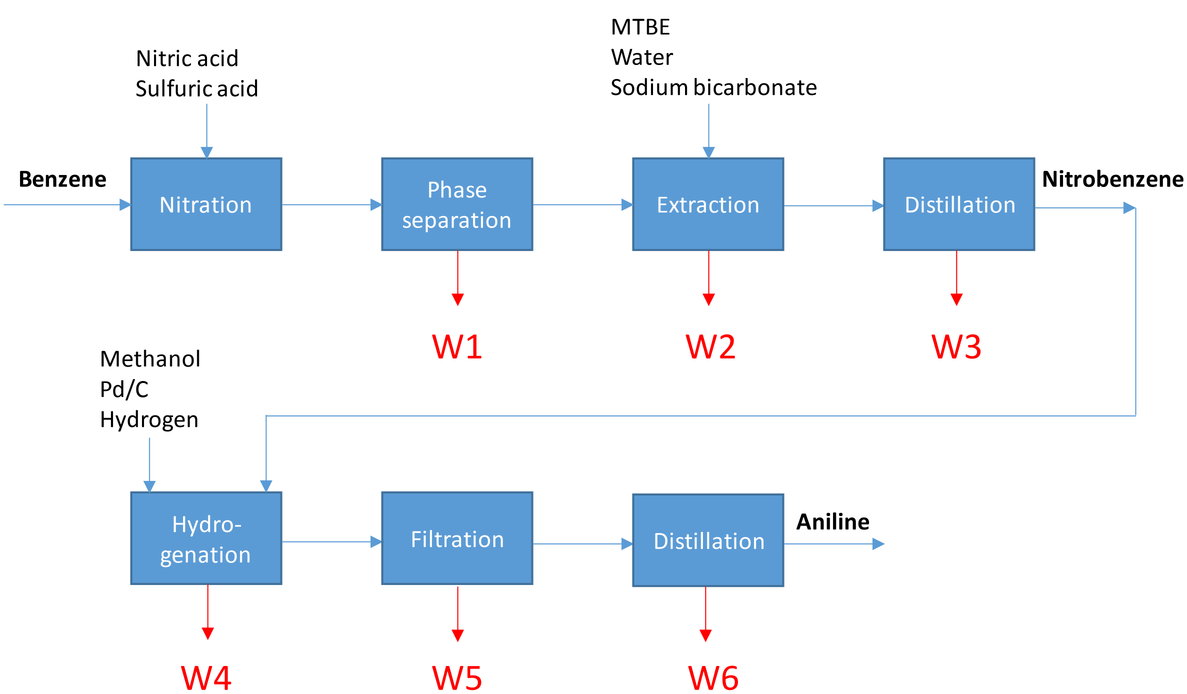
Quiz: Green chemistry / LCA

Green metrics & principles

Calculate the atom economy, carbon efficiency, reaction mass efficiency, generalized reaction mass efficiency and E-factor for the following synthesis of aniline. What type and amounts (estimated) of waste streams (in red on flow diagram) are produced? Propose ways of decreasing the E-factor. Identify and discuss some of the pros and cons of this process in the context of green chemistry.



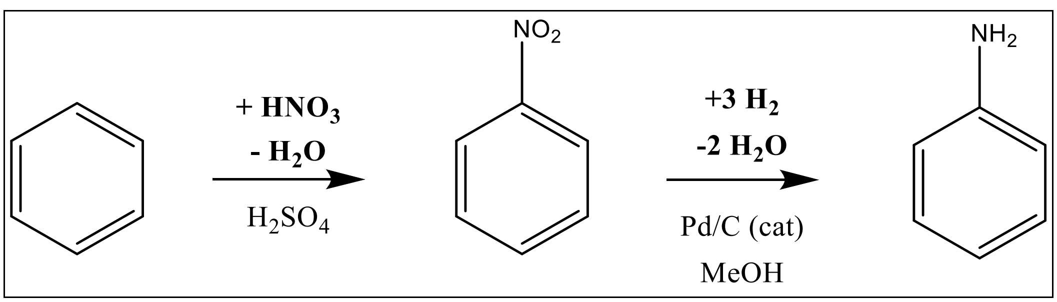


Nitration step		Purity (w/w)	MW (kg/kmol)	Mass (kg)
IN	Benzene	1	78.1	300
	Nitric acid	1	63.0	247
	Sulfuric acid	1	98.1	245
	Methyl tert-butyl ether	1	88.2	600
	Sodium bicarbonate	1	84.0	10
	Water	1	18.0	100
OUT	Nitrobenzene	0.987	123.1	469

Hydrogenation step		Purity (w/w)	MW (kg/kmol)	Mass (kg)
IN	Nitrobenzene	0.987	123.1	469
	Methanol	1	32.0	2200
	Hydrogen	1	2.0	26
	Pd/C		-	2.3
OUT	Aniline	0.97	93.1	358

Solution

Balanced equations



STEP			MW (kg/kmol)	Conc (w/w)	Mass (kg)	kmol
Nitration/phase sep	IN	**Benzene**	78.1	100.0%	**300**	3.84
Nitration/phase sep	IN	**Nitric acid**	63.0	100.0%	247	3.92
Nitration/phase sep	IN	**Sulfuric acid**	98.1	100.0%	245	2.50
Nitration/phase sep	OUT	**W1 (Acid waste)**			323	
Nitration/phase sep	OUT	**Crude Nitrobenzene**	123.1	98.7%	**469**	3.76
Extraction	IN	**Crude Nitrobenzene**	123.1	98.7%	**469**	3.76
Extraction	IN	**Water**	18.0	100.0%	100	
Extraction	IN	**Sodium bicarbonate**	84.0		10	
Extraction	IN	**MTBE**	88.2		600	
Extraction	OUT	**W2 (Aq wash)**			110	
Extraction	OUT	**Dil nitrobenzene**	123.1	43.3%	**1069**	3.76
MTBE distillation	IN	**Dil nitrobenzene**	123.1	43.3%	**1069**	3.76
MTBE distillation	OUT	**Nitrobenzene**	123.1	98.7%	**469**	3.76
MTBE distillation	OUT	**W3 Spent MTBE**			600	
Hydrogenation	IN	**Nitrobenzene**	123.1	98.7%	**469**	3.76
Hydrogenation	IN	**Methanol**	32.0		2200	-
Hydrogenation	IN	**Hydrogen**	2.0		26	13.18
Hydrogenation	IN	**Pd/C**	-		2.35	-
Hydrogenation	OUT	**W4 Hydrogen**	2.0		4	1.88
Hydrogenation	OUT	**Het rx mix**	93.1		2694	3.73
Filtration	IN	**Het rx mix**	93.1		**2694**	3.73
Filtration	OUT	**Crude Aniline**	93.1		2692	3.73
Filtration	OUT	**W5 Spent catalyst**			2.3	
Methanol distillation	IN	**Crude Aniline**	93.1		2692	3.73
Methanol distillation	OUT	**W6 Wet methanol**			2334	
Methanol distillation	OUT	**Aniline**	93.1	97.0%	**358**	3.73

Nitration acid waste (W1)

	MW	kmol	kg	w/w	Remarks
H2O	18.0	3.76	68	21.0%	kmol benzene*nitration yield
HNO3	63.0	0.15	10	3.0%	kmol initial-kmol consumed
H2SO4			245	76.0%	

H2O formed in Hydrogenation

kmol	7.45	(2* mol aniline)
kg	134.2	

Wet methanol composition (W6)

	kg	w/w
MeOH	2200	94.3%
H2O	134.2	5.7%

Waste name	kg	Description
W1	323	H2SO4 (76%), HNO3 (3%), water (21%), traces of nitrobenzene (water solubility~0.2%) and benzene (water solubility ~0.2%)
W2	110	Aqueous sodium bicarbonate (10%), traces of sodium sulfate, traces of nitrobenzene (water solubility~0.2%) and benzene (water solubility ~0.2%)
W3	600	MTBE, water, traces of nitrobenzene and benzene
W4	4	hydrogen, methanol, nitrobenzene, aniline
W5	2	Pd/C, methanol, water, aniline
W6	2334	Methanol (94%), water (6%), traces of aniline
Total	**3373**	

Atom economy	63%
Yield	97.0%
(organic) solvent intensity	7.83
CE	97.0%
RME	62%
gRME	10%
E-factor (incl. aqueous waste)	9.43

E-factor reduction:

- Reduce amounts of solvents
- Recycle solvents
- Optimize washing step (less water/solvent)

Pros:

Atom economy, short synthesis, catalytic steps, water as byproducts

Methanol ranked "In-between recommended and problematic"[1]. A rather acceptable solvent (except for its toxicity/flammability). Can be sourced renewably (bio-methanol).

Cons:

- Benzene and nitrobenzene both very toxic
- MTBE ranked "In-between problematic and hazardous"[1]. Potentially carcinogenic and cannot be sourced renewably. Consider replacing.
- High E-factor
- High solvent intensity
- Nitration step hazardous

Green chemistry & LCA questions

1. **Describe some advantages and limitations of the E-factor**

A good driver for the reduction of waste, thus of environmental impact

Not addressed: safety, environmental and human toxicity, renewability of raw materials, energy, nature of waste

2. **Describe some advantages and limitations of Reaction Mass Efficiency**

A good driver for the maximization of reaction efficiency, minimization of by-products and use of excess reactants.

Not addressed: solvent and workup materials, waste, environmental and human toxicity, safety, amounts of solvents, energy, renewability of raw materials

3. **Define "burden" in LCA**

The sum of emissions of a specific substance within the system's boundary

4. **Name and describe 4 impact categories in LCA**

[1] Byrne et al., Tools and techniques for solvent selection: green solvent selection guides, Sustain Chem Process (2016) 4:7

Global warming potential, Ozone layer depletion potential, Tropospheric ozone formation potential, Acidification potential

5. Give 2 examples of burden shifting

Fossil fuels → bio fuels to attempt decreasing GWP → increase of eutrophication potential and land use, loss of biodiversity, increase toxicity on freshwater ecosystems

Changing the purification sequence by postponing a distillation step further downstream in the manufacturing chain: shift of emissions from one plant to another.

6. Why can dimethyl carbonate be considered as a "green" reagent and solvent?

Green synthesis. Replacement of hazardous methylating agents (phosgene, dimethyl sulfate) using a clean process (catalytic, no solvent, no wastewater). Biodegradable. Not toxic.

7. Cite 2 substances causing water eutrophication

Ammonia, phosphoric acid

8. Cite 2 substances causing acidification

Sulfur dioxide, nitrogen oxides

9. Cite 2 substances causing global warming

CO_2, N_2O

10. Name the reference compound for acidification

SO_2

11. Which chemical is the main contributor to global warming worldwide?

CO_2

12. Does N_2O have a higher ozone depletion potential than CFC-11?

No, the ODP of CFC-11 is 59 times higher than N2O

13. Which sector is the largest contributor to global warming worldwide: transportation, energy, or manufacturing?

Energy (~50%)

14. What is the main environmental issue with CFCs and what is their mechanism of action?

Stratospheric ozone depletion → increased exposure to carcinogenic UV-B. Formation of chlorine radicals that catalyze the transformation of ozone to O_2. High stability of CFCs allow them to reach the stratosphere without being degraded

15. Which substance has the largest global warming potential: SF_6, CFC-11 or CO_2?

SF_6 by far

16. Calculate the photochemical ozone creation potential for a process that emits 2.2 kg of methane, 0.2 kg of propane and 0.1 kg of 2-methylhexane per ton of final product.

	kg / ton	POCP in kg ethylene / kg	kg ethylene-eq / ton
methane	2.2	0.034	0.075
propane	0.2	0.411	0.082
2-methylhexane	0.1	0.719	0.072
TOTAL			**0.229**

17. Cite three possible boundaries of a LCA

Cradle to grave, cradle to gate, gate to gate