Safe-and-Sustainable-by-Design redox active molecules for energy storage applications

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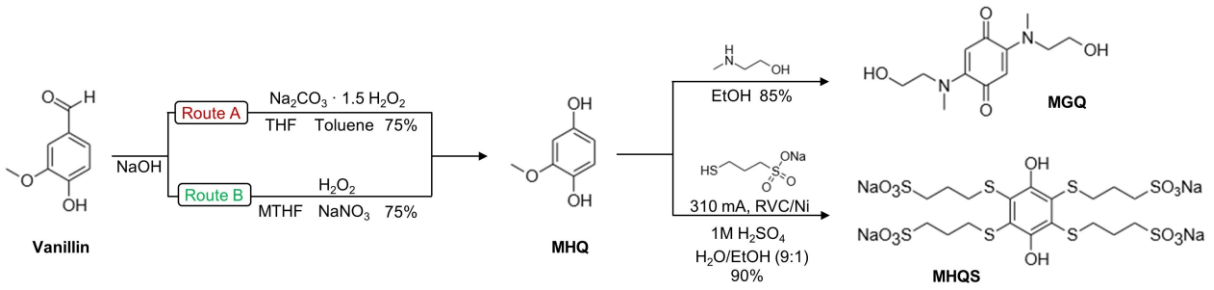
Keywords

Safe-and-Sustainable-by-Design, Safe-by-Design, redox flow battery, energy storage system, quinone, electrolyte, ecotoxicity, social life cycle assessment, life cycle assessment;

Supplementary information

Synthesis of quinones

Two methods were used to prepare 2-methoxyhydroquinone (MHQ, oxidized form 2-methoxy-1,4-quinone (MQ)) from vanillin (Supplemental Figure 1) [1, 2]. In the first, commercially available sodium carbonate peroxide was used as an oxidizer and tetrahydrofuran (THF) as solvent. The rapid reaction of vanillin with hydrogen peroxide under alkaline conditions produced MHQ in high yields of 75.8% [2]. In an alternative approach, the solvent was replaced by 2-methyltetrahydrofuran (MTHF), producing MHQ with basically the same yield (75%). To prepare 2,5-bis(*N*-methylethanolamino) cyclohexa-2,5-diene-1,4-dione (MGQ), MHQ was treated with *N*-methylethanolamine in ethanol (85%). Thioether-substituted hydroquinone (MHQS) was obtained with 90% yield in electrochemical oxidation of MHQ in presence of sodium 3-mercaptopropylsulfonat [3, 4]. Both reactions were performed in a multigram scale. A detailed description of the processes and characterization can be found in the supplemental information (Supplemental Figure 2-4).



Supplemental Figure 1: Synthesis of MHQ from vanillin and subsequently MGQ and MHQS. The percentages shown represent the yield values of the corresponding pathways.

Vanillin (≥99%), sodium percarbonate (≥99.0%), sodium nitrate (≥99.0%), 2-(methylamino)ethanol (≥98%) and sodium 3-mercapto-1-propylsulfonate (90%) were purchased from Merck KGaA (Darmstadt, Germany). $CDCl_3$ (99.9%), DMSO-d_6 (99.8%) and D_2O (99.9%) were purchased from Eurisotop SAS (St. Aubin, France). Sodium hydroxide (≥98%), hydrogen peroxide (30%) and sodium sulfate (≥99.0%) were purchased from Carl Roth GmbH (Karlsruhe, Germany). ^1H (300 MHz), ^{13}C (75 MHz), and Heteronuclear multiple-bond correlation (HMBC)-NMR spectra were recorded on a Bruker

Avance III 300 MHz with an autosampler. Infrared spectra were obtained on a Bruker Alpha-P Diamond ATR spectrometer from solid sample. UV/VIS spectra were recorded with an Agilent Cary 60 UV/Vis spectrometer. Melting points were determined by a Stuart automatic melting point (SMP50). Cyclic voltammograms (CVs) were carried out using a BioLogic SP 150 potentiostat/galvanostat and analyzed using ECLab software. A VC 4 Voltammetry cell (ALS Co.) with a glassy carbon working electrode (GCE; GC6x3, ALS Co., 3 mm diameter), a platinum wire as counter electrode and an Ag/AgCl (RE 1B, 3 M NaCl, ALS Co.) reference electrode (E^0 = 195 mV vs SHE) was used. The working electrode was polished using a 0.05 µm alumina polishing solution and polishing pad (PK 3 Electrode Polishing kit, ALS Co.) prior to each measurement and a 1 µm diamond polishing solution if necessary. The electrolyte solutions were degassed by bubbling nitrogen through the solution for at least 10 minutes before measurement.

2-Methoxyhydroquinone (MHQ)

Route A: MHQ was synthesized according to a procedure described by Schlemmer and colleagues using tetrahydrofuran (THF) as solvent [2].

Route B: 0.6 g (5.7 mmol) Na_2CO_3 and 80 mg (0.2 mmol) NaOH dissolved in 15 ml of distilled water were placed in a 100 mL round bottom flask. Afterwards, 1.75 g (20.6 mmol) $NaNO_3$ were added to the colorless solution. 7 mL (22.9 mmol) of a 106.78 g/L H_2O_2 solution were added, cooled to 10°C and stirred for 10 min at 300 rpm. Then, 0.8 g (5.3 mmol) vanillin dissolved in 10 mL of 2-methyltetrahydrofuran (MTHF) were added. After stirring for several minutes, the organic phase was separated, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The product was purified by sublimation at 80 °C and 10 mbar, giving rise to a yield of 0.58 g (75%). ^{1}H-NMR (400 MHz, CD_3OD): δ = 6.62 (d, 1H, $^3J_{HH}$ = 8 Hz), 6.43 (d, 1H, $^3J_{HH}$ = 4 Hz), 6.24 (dd, 1H, $^3J_{HH}$ = 5.6 Hz, $^3J_{HH}$ = 2.8 Hz), 3.79 (s, 3H). ^{13}C-NMR (101 MHz, CD_3OD): δ = 150.46 (C-1), 148.17 (C-3), 139.01 (C-4), 115.07 (C-5), 106.17 (C-6), 99.98 (C-2), 54.88 (C-7) ppm. ^{1}H-^{13}C HMBC (400 MHz, CD_3OD) 6.62:150.46, 6:62:148.17, 6.62:139.01, 6.62:99.98, 6.24:150.46, 6.24:148.17, 6.24:139.01, 6.24: 115.07, 6.24:106.17, 6.24:150.46, 6.24:139.01, 6.24:99.98, 3.79:148.17.

2,5-bis(*N*-methylethanolamino) cyclohexa-2,5-diene-1,4-dione (MGQ)

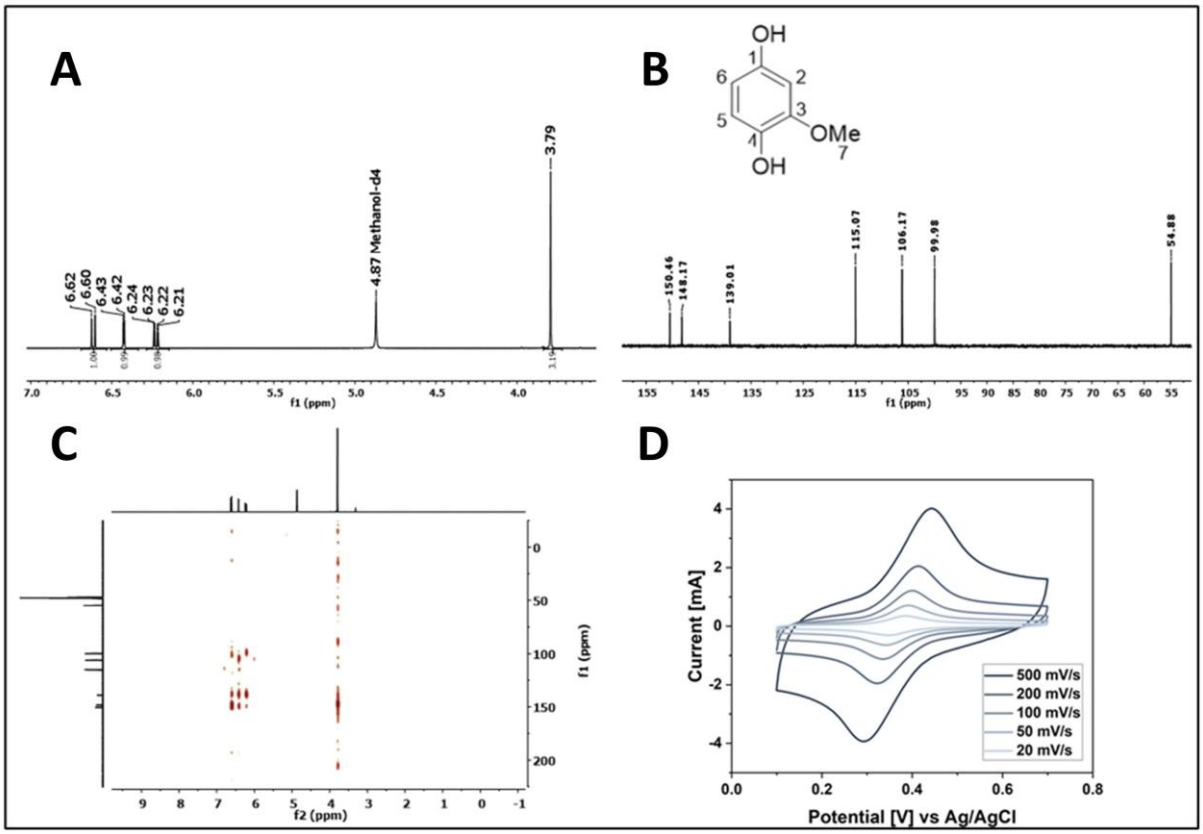
MHQ (5 g, 36 mmol, 1 equiv.) was dissolved in ethanol and stirred for 15 min. Then, 5.9 g (79 mmol, 2.2 eq.) of *N*-methylethanolamine (NMEA) were slowly added to the reaction mixture at 25°C and stirred for 24 hours. The reaction progress was monitored using thin layer chromatography (TLC). Upon completion the product precipitated. After filtration it was washed with ice-cold ethanol to obtain red crystals (dark-red solid, m.p.: 160-162 °C) with a yield of 7.5 g (85%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.28 (s, 2H), 4.74 (s, 2H), 3.77 (t, *J*= 5.4 Hz,-4H), 3.57 (t, *J*= 5.4 Hz, 4H), 3.02 (s, 6H), ^{13}C NMR (75 MHz, DMSO-d_6) δ 180.67 (C-1, *C*=O), 151.78 (C-2), 101.24 (C-3), 59.41 (C-6), 55.73 (C-5), 41.40 (C-4, -*C*H_3), ^{1}H-^{13}C HMBC (300 MHz, DMSO-d_6) δ 5.28:180.67, 5.25:151.78, 3.77:151.78, 3.77:59.41, 3.77:55.73, 3.77:41.40, 3.57: 55.73, 3.02:151.78, 3.02:101.24, 3.02:55.73 ppm.

IR [cm^{-1}]: 3303 (s, OH-stretch), 2930 (C-H stretch), 1612 (m, C=O stretch), UV-Vis: λ [nm] (ε [L mol^{-1} cm^{-1}]) = 507 (653), 365 (23860).

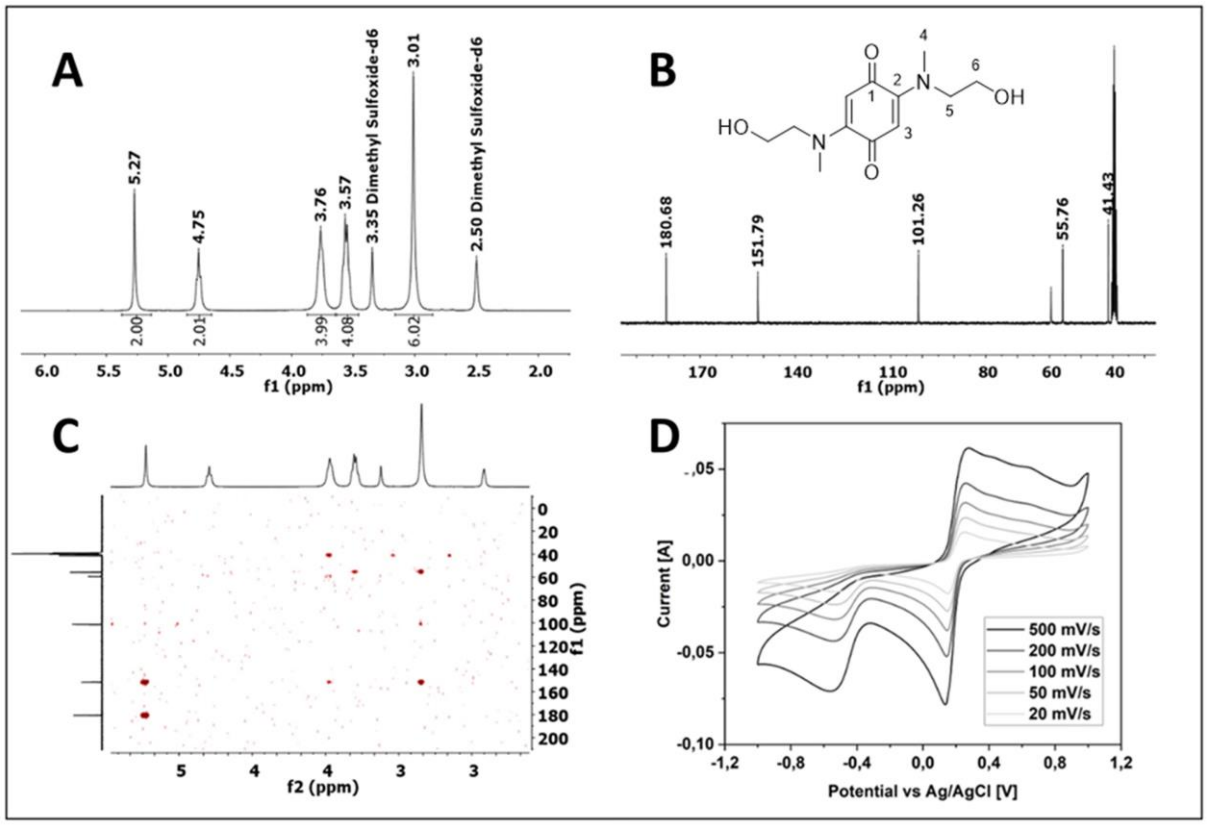
Tetrathioether hydroquinone (MHQS, 3,3',3'',3'''-((3,6-dihydroxybenzene-1,2,4,5 tetrayl)tetrakis (sulfanediyl))tetrakis(propane-1-sulfonate)

The reaction was performed according to a modified procedure reported by Stahl and colleagues [3, 4]. In a 250 ml beaker, MHQ (5 g, 37 mmol) was dissolved in 200 mL of a water/ethanol mixture (9:1). Sodium 3-mercaptopropylsulfonate (MPSNa, 90% technical grade, 28.26 g, 143 mmol) was added and stirred until dissolved. Aqueous sulfuric acid (1 M, 2 mL, H_2SO_4) was added. Reticulated vitreous carbon (RVC) was used as an anode and a nickel wire as the cathode. A current of 310 mA passed without stirring. The reaction time was calculated using Faraday's law of electrolysis. The electrodes were rinsed with small portions of water. About two thirds of the solvent were removed using a rotary evaporator. Afterwards, cold ethanol was added slowly until precipitation was observed. After 0.5 hours the precipitate was filtered and rinsed with cold ethanol. The solid was dried overnight in a vacuum oven at 40°C to yield 26 g (120 mmol, 90% yield) of the product as a white solid. ^{1}H NMR (300 MHz, D_2O) δ 3.06 (m, 4H), 1.93 (m, 2H) ppm, ^{13}C NMR (75 MHz, D_2O) δ 152.6 (C-1), 126.3 (C-2), 49.9 C-

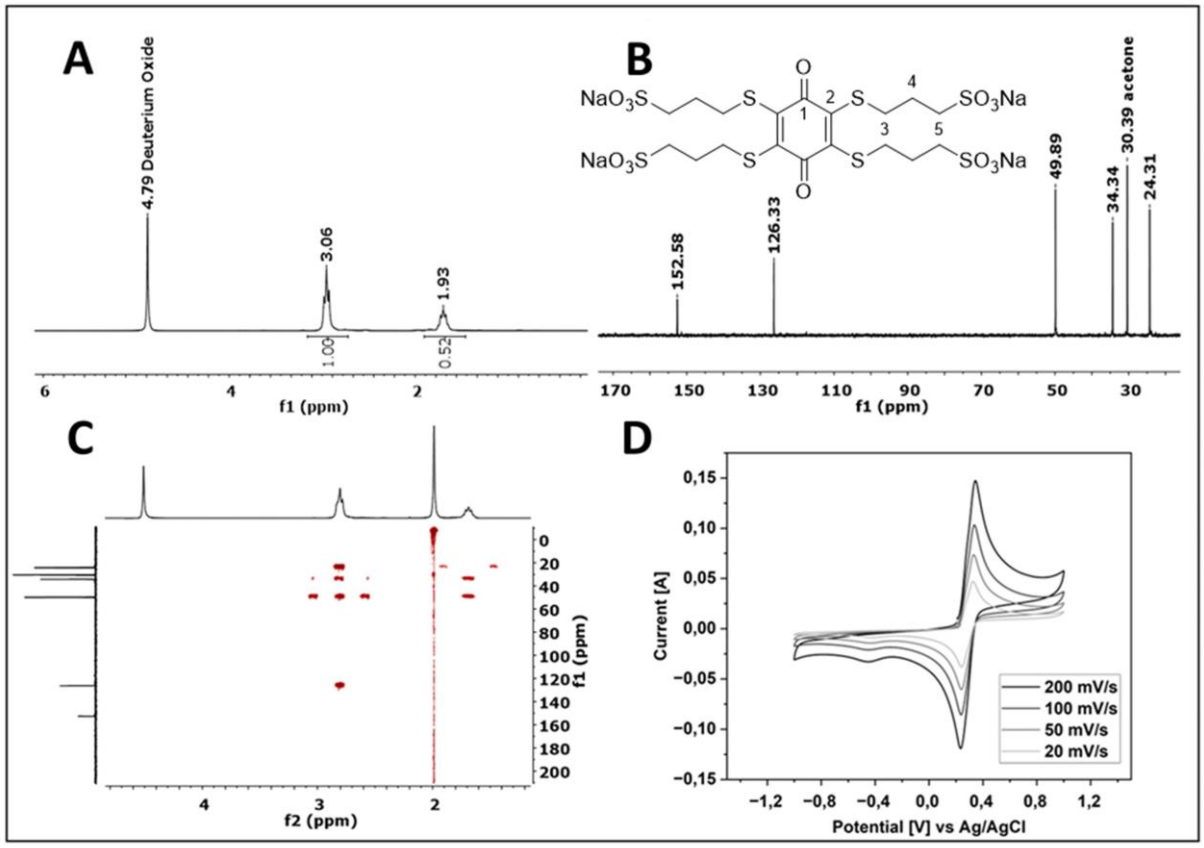
5), 34.3 (C-4), 24.3 (C-3) ppm, ^{1}H-^{13}C HMBC (300 MHz, D_2O) δ 3.06:126.3, 3.06:49.9, 3.06:34.34, 3.06:24.3, 1.93:34.3, 1.93:49:9 ppm.



Supplemental Figure 2: Characterization of MHQ. (A-C) 1H, 13C and 1H-13C HMBC NMR spectra of MHQ. (D) Cyclovoltammetric investigation of MHQ in 0.5 M H3PO4 (pH 1.23) with c ≈ 1 mg/mL (7.1 mM). 5 scan rates from 500 to 20 mV s-1 were used: 500, 200, 100, 50, 20 mV s-1 1. E0´ (redox potential): 345 mV ± 2 mV vs Ag/AgCl (averaged over scan rates).



Supplemental Figure 3: Characterization of MGQ. (A-C) ^{1}H, ^{13}C and ^{1}H-^{13}C HMBC NMR spectra of MGQ.(D) Cyclovoltammetric investigation of MGQ in 0.5 M H_3PO_4 (pH 1.23) with c ≈ 1 mg/mL (3.9 mM). 5 scan rates from 500 to 20 mV s^{-1} were used: 500, 200, 100, 50, 20 mV s^{-1} 1. $E^{0'}$ (redox potential): 204 mV ± 2 mV vs Ag/AgCl (averaged over scan rates).



Supplemental Figure 4: Characterization of MHQS. (A-C) ^{1}H, ^{13}C and ^{1}H-^{13}C HMBC NMR spectra of MHQS. (D) Cyclovoltammetric investigation of MHQS in 0.5 M H_3PO_4 (pH 1.23) with c ≈ 1 mg/mL (1.2 mM). 4 scan rates from 200 to 20 mV s^{-1} were used: 200, 100, 50, 20 mV s^{-1} 1. $E^{0'}$ (redox potential): 365 mV ± 2 mV vs Ag/AgCl (averaged over scan rates).

Ecotoxicity testing

Ecotoxicity testing was performed using *Daphnia magna* following OECD Test No. 202 and US-EPA OCSPP 850.1010 [5, 6], which were cultured in a 2 L aquarium at a stock density of 50 neonates/tank, under a photoperiod of 16/8 hour light/dark cycle, pH 7.9 ± 0.2, conductivity 641.1 ± 30.0 µS and 249.4 ± 35.5 mg of $CaCO_3$/L water hardness. Cultures were renovated monthly [7].

For *Daphnia* immobilization dose-range finding (DRF) experiments we employed neonatal daphnids (24 hours or younger). To obtain neonates, all neonates were removed from the culture stock tanks the day before starting the assay. The day of the assay, neonates were collected from intermediate tanks into fresh M4 media and kept in petri dishes at 20°C until the start of exposure. Polypropylene flasks (75 mL) were loaded with 60 mL of ELENDT M4 medium, a high-hardness media currently recommended for OECD testing. Using a Pasteur pipette, drops containing 5 individual daphnids were then transferred from petri dishes to each flask. Flasks were closed tightly and covered with aluminum

foil. No feeding was provided during the exposure duration. Flasks were positioned horizontally at 20°C. After 48 hours of exposure to the test item, daphnid immobilization was recorded. For this, flasks were gently shaken and movement of the 5 daphnids was monitored for 15 consecutive seconds. Daphnids were considered immobilized if unable to swim/move during this period. Once analyzed, daphnids were euthanized by 10 % sodium hypochlorite and eliminated under the laboratory waste requirements. Also, any presence of precipitation in the test vial was reported.

Based on these DRF results, concentrations for the definitive *Daphnia* immobilization assay were defined. The test concentrations are depicted in Supplemental Table 1. Since no immobilization occurred at the highest tested concentrations for the DRF for MGQ and MHQS, the test concentrations for the definitive test were elevated to maximum feasible test concentrations (based on maximal solubility). The percentage of immobilized daphnids was calculated for each test condition. Statistical analysis was carried out to model a concentration-response curve with the obtained percent immobilized individuals using non-linear regression analysis. The software GraphPad Prism calculated the EC50 values for the 48 hours measurement, along with the respective 95% confidence intervals and the graphical plot shown in Figure 4 and 5.

Supplemental Table 1: Overview of the test concentrations for the definitive Daphnia immobilization assay.

Test substance	**Test concentrations for definite test**
MHQ	0.01, 0.03, 0.01, 0.2, 0.5, 1.3, 3.5, 9.0 nM
MQ	0.004, 0.01, 0.03, 0.1, 0.2, 0.5, 1.2, 3.2 nM
MGQ	20, 39, 78, 156, 313, 625, 1250, 2500 µM
MHQS	8, 16, 31, 63, 125, 250, 500, 100 µM

Supporting Info for streamlined LCA

Supplemental Table 2 shows data used for streamlined LCA.

Supplemental Table 2: Aggregated cradle-to-gate inventories for the production of 1 kg electrolyte that contains 20 wt% kraft lignin-derived MHQ (Route B; LCI data based on the works of Culbertson et al. 2016 [8]; Khwanjaisakun et al. 2020 [9]; Wongtanyawat et al. 2018 [10]; as well as own experimental data regarding MHQ production)

Aggregated inputs	**Amount**	**Unit**
Electricity (market mix)	39.60	kWh

Cooling energy (natural gas)	143.69	MJ
Heat (natural gas)	168.71	MJ
Kraft lignin	3.74	kg
Sodium hydroxide	4.98	kg
Sulfuric acid	6.11	kg
Hydrogen peroxide	0.11	kg
Ethyl acetate	0.09	kg
Nitrogen, liquid	0.49	kg
Tetrahydrofuran	0.02	kg
Oxygen, liquid	0.13	kg
Phosphoric acid	0.07	kg
Water	128.35	kg
Sodium nitrate	0.00	kg
Sodium sulfate (avoided b., subtract)	-8.45	kg

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