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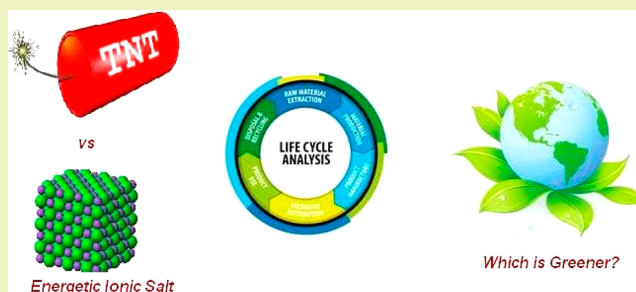
# Energetic Ionic Materials: How Green Are They? A Comparative Life Cycle Assessment Study

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**ABSTRACT:** Recently, several energetic ionic salts and liquids have been proposed as novel high-energy materials, propellants, and explosives. The life cycle environmental impacts of these new energetic salts have not been previously studied. Environmental impacts arise both from release of these energetic materials themselves as well as from their synthesis. In this work, for the first time, we report the results of cradle-to-gate life cycle environmental impacts of production of energetic ionic salt 1,2,3-triazolium nitrate and compare it with traditional energetic material 2,4,6-trinitrotoluene (TNT). The results indicate that the production processes of ionic salt have a significantly higher environmental footprint than conventional energetic materials. The above result was consistent across all nine impact categories analyzed and can be directly attributed to energy intensive steps needed to prepare the ionic salt and its precursors. The findings suggest that ionic energetic materials have higher environmental impact than TNT from a life cycle perspective.

**KEYWORDS:** Life cycle assessment, Ionic salts, Energetic materials



## INTRODUCTION

Energetic materials are used as explosives or as fuels. They release a large amount of energy when they decompose. In the case of explosives all energy is released rapidly while in the case of fuels energy is released in a controlled manner. These materials derive their energy content from oxidation of the carbon backbone or from their high positive heats of formation. The general requirements for energetic materials are high energy density, thermal stability, low sensitivity to impact, and low toxicity.<sup>1</sup> Traditional energetic materials that are commonly used in explosive formulations are HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), and TNT (2,4,6-trinitrotoluene).<sup>2</sup> Hydrazine derivatives are widely used as energetic fuel in rocket propulsion systems.<sup>3,4</sup> When discharged to the environment energetic materials will interact with biological systems. Use of energetic materials such as TNT and RDX can leave residues which can potentially impact environmental and human receptors.<sup>5</sup> Monitoring studies reveal that some of these munition compounds persist at the sites where they were produced or processed.<sup>6</sup> Unexploded and low-order detonation residues containing TNT, RDX, and HMX have been pointed out as the main source of groundwater contamination in military training ranges.<sup>7</sup> Indeed, munition compounds, such as RDX, have been detected in sole-source drinking water aquifers in military ranges such as Camp Edwards.<sup>8</sup> These chemicals have been found to be moderately to highly toxic to freshwater organisms.<sup>5</sup> In addition low concentrations of explosive compounds have been measured in marine sediments.<sup>9</sup>

With an aim to address some of the above environmental concerns researchers are exploring other *green* energetic material formulations. There is growing interest in the development of new energetic ionic salts and liquids for use as aerospace propellants and explosives.<sup>3</sup> As energetic materials, ionic salts offer several advantages over conventional energetic molecular compounds that include negligible volatility (ease of handling) and high density.<sup>2</sup> Energetic ionic salts can be prepared by combining energetic cations such as 1,2,3-triazolium with energetic anions such as nitrates, perchlorate, and dinitramide.<sup>10</sup> The high heats of formation of these salts are primarily due to the presence of nitrogen containing cations and anions.<sup>2</sup> Nitrogen-rich heterocyclic energetic salts are of particular interest.<sup>11–19</sup> A large number of ionic salts that are based on a triazole derivative have been proposed as energetic materials.<sup>16–19</sup> Triazole has a molecular formula of  $C_2H_3N_3$  with a five-membered ring that contains three nitrogen atoms located at the 1,2,3 or 1,2,4 positions. 1,2,4-Triazole and 1,2,3-triazole have heats of formation values of 109 and 272 KJ/mol, respectively.

As discussed previously, one of the main driving forces for the discovery and development of new energetic materials, such as ionic salts, is the mitigation of environmental and toxicological hazards associated with currently used materials. Manufacture of chemicals through environmentally friendly

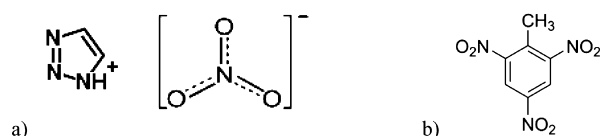
**Received:** November 12, 2012

**Revised:** February 6, 2013

**Published:** February 20, 2013

approaches represents a fundamental industrial challenge. The energetic ionic salts possess lower vapor pressures and higher densities compared to nonionic molecules.<sup>2</sup> Due to their negligible vapor pressure, they are usually considered as “green” alternatives to volatile molecular compounds. In addition, ionic salts have tunable physical and chemical properties that enable us to tailor their structures for task specific applications such as energetic materials. Since ionic liquids and salts are of inherently less risk to human health and the environment they are considered as green chemicals. However, a more fundamental definition of green chemistry involves reducing or eliminating the use or generation of hazardous substances in the design, manufacture, and application of chemical products.<sup>20</sup>

In order to legitimately evaluate the greenness of ionic salts as energetic materials, it is not enough to consider the inherently benign nature of the chemical, we also need to take a holistic view that considers environment and health impacts associated with the entire life cycle of their production including direct environmental emissions during the production phase and indirect emissions associated with energy use in their production. This article presents the first comprehensive cradle-to-gate life cycle assessment that considers all stages involved in production of 1,2,3-triazolium nitrate, a triazole based energetic ionic salt, and compares it with the environmental impact associated with production of TNT on a functional unit basis. This approach will allow us to systematically investigate whether ionic salt based energetic materials provide any environmental benefits in comparison to traditional energetic materials. The chemical structure of 1,2,3-triazolium nitrate and TNT are shown in Figure 1.



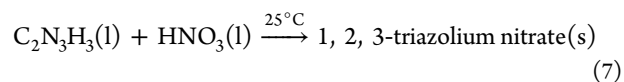
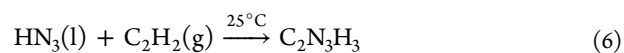
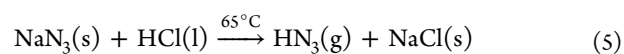
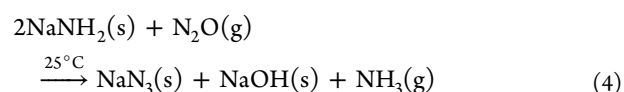
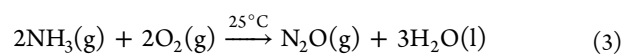
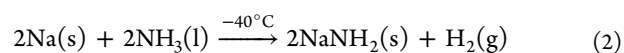
**Figure 1.** (a) 1,2,3-Triazolium nitrate. (b) TNT.

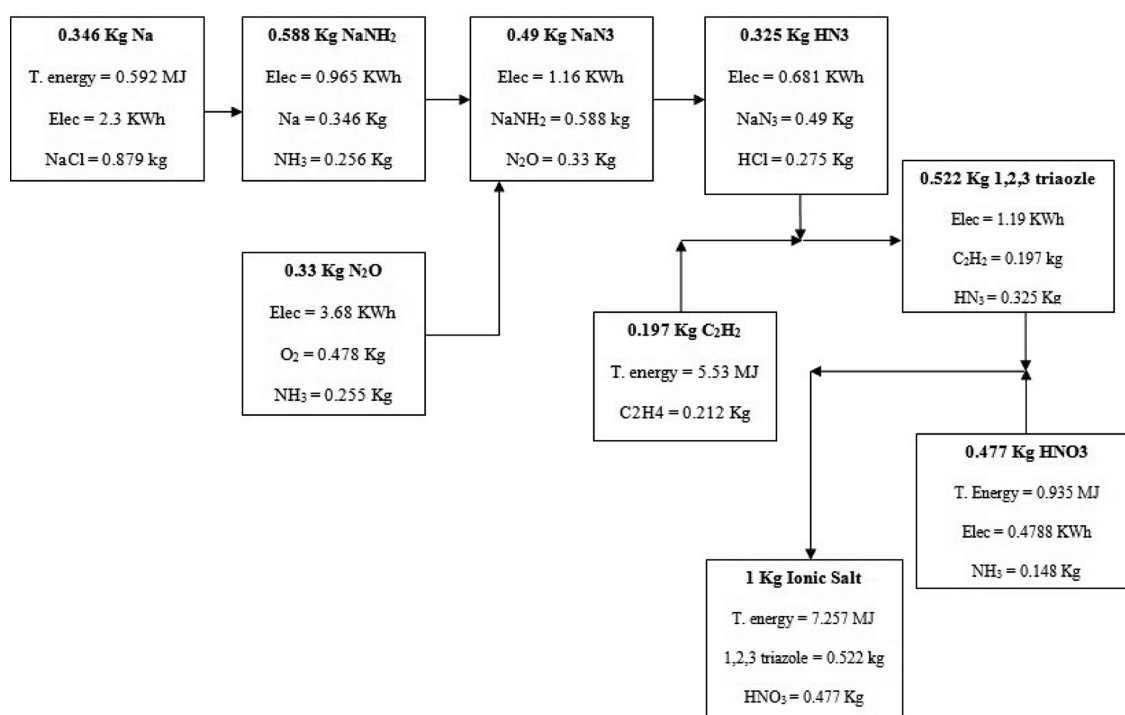
There are several challenges involved in performing a life-cycle assessment (LCA) of ionic salts. Most of these challenges are due to the fact that ionic salts are a new class of compounds that are emerging. Ionic salts are not yet produced in large scales in commercial plants, and there is no primary data available on material/energy consumption and direct environmental discharges. Process design and simulation software cannot be used to model production processes of ionic salts due to a lack of comprehensive physical and thermodynamic property models for these salts and their precursors. Therefore, simulation of material and energy balances of ionic salt production processes becomes very difficult. The other important challenge in modeling environmental impacts is that there are no emission factors available in LCA databases such as Ecoinvent and Gabi for several precursors (reactants) that are required for IL production. Due to these limitations, no LCA study has been done on ionic salts. To our knowledge, even for ionic liquids, there have been only few LCA studies that have considered them in their analysis.<sup>21–23</sup> In order to overcome the above-mentioned challenges, we use a theoretical approach to estimate theoretical energy requirements for reaction and separation steps involved in ionic salt production. Then, we adjust the theoretical energy requirements to actual

energy consumption by accounting for energy losses through the use of data from a comparable industrial process. Direct discharges of the ionic salt and its precursors to the environment during the production phase are assumed to be negligible. This energy and associated environmental loads constitute the inventory for the LCA method.

### Process and Energetic Requirements for Triazolium Nitrate Synthesis. Synthesis of 1,2,3-Triazolium Nitrate.

The main reaction for synthesis of triazolium nitrate proposed by Drake et al.<sup>1</sup> and shown in eq 7 is adopted for this paper. However, the emission factors (life-cycle emissions) for the reactants involved are not available in standard LCI databases such as Ecoinvent. Therefore, we consider a series of upstream reactions (eqs 1a–6) that constitute the *life-cycle tree* for the production of ionic salt 1,2,3-triazolium nitrate. We calculate theoretical energy requirements for each of these steps that are part of the reaction tree. Major energy consumption in these batch processes would relate to the reaction and separation stages. Wherever appropriate, we make further assumptions of minimal separation energy requirements (and therefore ignore them) when the products are in two different phases (easy to separate) or the product is of high yield (no need to separate small quantities of byproduct). Actual industrial scenarios involving potential future scale-up are expected to be more energy intensive, as in an industrial plant the actual energy consumption is few times greater than theoretical energy requirements due to heat and energy losses. To capture this effect, we did a comprehensive review of several studies and found this factor to vary between 3 and 5 times that of theoretical energy requirement. In order to make an adjustment, we selected a comparable process (synthetic production of sodium carbonate) for which industrial energy consumption data was available.<sup>24</sup> We calculated the theoretical energy requirement for this process, compared it with actual energy consumed, and found that actual electricity consumption is 3.2 times higher than theoretical electricity requirement while actual natural gas consumption is 4.2 times higher than theoretical natural gas requirements. We also assume that for exothermic reactions electricity is used for cooling and for endothermic reactions natural gas is used for heating. We use the two correction factors in all our calculations to transform theoretical energy requirement to actual energy consumption.





**Figure 2.** Material and energy flows associated with the life cycle tree for producing the ionic salt 1,2,3-triazolium nitrate.

The production of sodium is based on a well-known electrolysis cell process (eq 1a and 1b). The potential required to oxidize  $\text{Cl}^-$  ions to  $\text{Cl}_2$  is  $-1.36$  V, and the potential needed to reduce  $\text{Na}^+$  ions to sodium metal is  $-2.71$  V. Therefore, a potential of at least  $4.07$  V is required to drive this reaction.<sup>25</sup> In the second step, sodium (solid) and ammonia (gas) are reacted at  $375$  °C to produce sodium amide and hydrogen (eq 2).<sup>26</sup> Sodium amide is in liquid phase, and hydrogen is in the gas phase at this temperature. Thus, we assume that the energy requirement for separation of the two phase products in a small scale batch plant is equal to the energy required for cooling sodium amide from reaction temperature to room temperature. We calculated the theoretical heat of reaction as  $-2.12$  MJ/kg, and the theoretical heat of separation as  $0.634$  MJ/kg. Accounting for correction factors, this translates into a total cooling load requirement of  $2.0448$  kW h per kg ionic salt and total heating load of  $2.66$  MJ per kg ionic salt (equivalent to  $0.0616$  m<sup>3</sup> of natural gas/kg). In the next step, ammonia (gas phase) and oxygen are reacted at room temperature, to produce nitrous oxide and water (eq 3). Nitrous oxide is in the gas phase and water is in the liquid phase at this temperature. Thus, we assume no significant energy requirement for separation in a small scale batch plant. We calculated the theoretical heat of reaction to be  $-15.47$  MJ/kg. Accounting for correction factors this translates to  $11.162$  kW h per kg ionic salt.

In the next step, sodium amide (solid phase) and nitrous oxide are reacted at  $200$  °C, to produce sodium azide (solid phase), sodium hydroxide (solid phase), and ammonia (gas phase). The energy requirement for separation stage is based on solid–solid separation of the two solid products, and the theoretical heat of reaction was  $-3.295$  MJ/kg. Accounting for correction factors, the total cooling load requirement translates to  $2.87$  kW h/kg and total heating load requirement translates to  $2.60$  MJ/kg ( $0.0602$  m<sup>3</sup> of natural gas per kg of sodium azide). In the next step sodium azide (solid phase) is reacted with hydrochloric acid (liquid phase) at  $65$  °C, to produce

hydrazoic acid ( $\text{HN}_3$ ) and sodium chloride salt.<sup>27</sup> Since one of the products is a gas and the other a solid, the two phases can be separated through a one step flash drum. Therefore, we assume that for a batch plant the energy required for separation is minimal. We calculated the theoretical heat of reaction to be  $-2.9$  MJ/kg. Accounting for the correction factor, this translates to  $2.096$  kW h/kg ionic salt. In the next step, hydrazoic acid ( $\text{HN}_3$ ) and acetylene gas are reacted at  $25$  °C, to produce 1,2,3-triazole ( $\text{C}_2\text{N}_3\text{H}_3$ ).<sup>28</sup> The yield for this reaction is 99%. In view of very high yield (low unreacted materials) and presence of no important byproducts, for all practical purposes, 1,2,3-triazole ( $\text{C}_2\text{N}_3\text{H}_3$ ) can be considered pure. Thus, we assume no significant energy is required for separation. We calculated the theoretical heat of reaction as  $-2.275$  MJ/kg. Accounting for correction factor, this translates to  $3.68$  kW h per kg ionic salt. In the next step 1,2,3-triazole ( $\text{C}_2\text{N}_3\text{H}_3$ ) and nitric acid ( $\text{HNO}_3$ ) are reacted at  $25$  °C, to produce 1,2,3-triazolium nitrate (the energetic salt) with a yield, 98.9%. Due to high yield of reaction (very low nonreacted materials) and no important byproducts, the product can be considered as a pure component. Thus, we assume no significant energy is required for the separation part and the main energy consumption is the reaction phase. We calculated the theoretical heat of reaction as  $+1.73$  MJ/kg. Accounting for correction factor, this translates to  $7.27$  MJ/kg of ionic salt ( $0.168$  m<sup>3</sup> natural gas per kg of ionic salt). The entire energy and material balance of the life cycle tree to produce 1 kg of the ionic salt is shown in Figure 2.

**Synthesis of TNT.** TNT production is based on the synthesis procedure reported by Urbanski<sup>29</sup> In the considered process toluene and nitric acid are reacted at  $80$  °C (both in liquid phase) to give  $\alpha$ -,  $\beta$ -, and  $\gamma$ -trinitrotoluene (TNT). The industrial results show that 95% of the product is  $\alpha$ -TNT and the rest is distributed between  $\beta$ -TNT and  $\gamma$ -TNT. We assume that the major energy requirements for TNT production relates to the reaction step and separation step (separation of  $\alpha$ -TNT



Table 1. Impact of Ionic Salt and TNT (functional unit: 1 MJ energy content)

category	units	ionic salt	TNT
global warming	kg CO <sub>2</sub> eq	29.4738851	9.07309769
acidification	kg H <sup>+</sup> mole eq	9.489402937	3.752113828
HH criteria	kg PM <sub>10</sub> eq	0.023712006	0.007939867
eutrophication	kg N eq	0.0028481	0.00143745
smog	kg O <sub>3</sub> eq	1.588845	0.777182
ecotoxicity	CTU-eco	0.111861804	3.3806 × 10 <sup>-6</sup>
human health (cancer)	CTU-cancer	2.47276 × 10 <sup>-11</sup>	6.34994 × 10 <sup>-12</sup>
human health (noncancer)	CTU-noncancer	6.26146 × 10 <sup>-12</sup>	1.60791 × 10 <sup>-12</sup>

from byproducts). The theoretical energy requirement for the reaction step equals the heat of reaction calculated as −1.768 MJ/kg. The actual energy consumed by accounting for energy losses was estimated using comparable plant data as described previously. The estimated actual electricity requirement for cooling in reaction and separation steps is 2.638 kWh per kg TNT. The energy requirement for separation purposes has been predicted to be 0.902 MJ/kg.

**Life Cycle Assessment (LCA) of Energetic Ionic Salts.** *Functional Unit.* Energy content is the most appropriate functional unit for this comparative study. 1,2,3-Triazolium nitrate and TNT have different energy content, and their energy release mechanism also differs. While energy release from TNT is based on oxidation, the ionic salt relies on heat of formation. Therefore, the heat of combustion for TNT and heat of formation for ionic salt were used as measures of energy content. A reference of 1 MJ energy content was used as the basis of comparison. On a mass equivalence basis this translates, to the following reference flow: 1 kg of TNT is equivalent to 1.62 kg of ionic salt.

*System Boundary.* The system boundary includes the final step of ionic salt production (reaction and separation), upstream reaction/separation steps for the precursors (as defined by the reaction tree), electricity and natural gas production, and upstream processes involved in electricity and natural gas production including raw-material extraction and transportation.

*Life-Cycle Inventory.* Life-cycle inventory (LCI) represents the collection of data on the material and energy inputs and emissions associated with the production of the energetic ionic salt. Material and energy flows constructed in the previous section were used as inputs to the life-cycle inventory (LCI). Since the majority of processes are either new for which industrial scale-up has not been developed or physical, chemical, and thermodynamic properties of the precursors are not available and hence chemical process simulation was not possible, we used data from the approach outlined in the previous section as inputs to the inventory. Due to the challenges associated with performing an LCA of new chemicals—that were outlined earlier—we consider this simplified approach as adequate for the scope of this study. Emission factors for production of electricity, natural gas, and other starting materials of the life-cycle tree were obtained from the U.S. life-cycle inventory database.<sup>30</sup> The emission factor for electricity from grid was assumed as 70% generation from bituminous coal and 30% generation from natural gas, based on 2008 U.S. grid electricity data.<sup>31</sup> Since contribution of other renewable energy and nuclear sources to the grid were either very small or vary significantly depending on the location, we assumed all grid electricity is from coal and natural gas. Emission factors for electricity production from bituminous

coal included emissions from coal mining and transport and emissions from power plant. Emission factors for electricity production from natural gas (NG) included emissions from NG extraction from ground and transport, emissions from NG processing and emissions from power plant. Emission factors for natural gas combustion include emission from NG extraction from ground, emissions from NG processing, and emissions from NG combustion in an industrial boiler. Life cycle emission factors for some of the materials in the life cycle tree (sodium chloride [NaCl], ammonia [NH<sub>3</sub>], oxygen [O<sub>2</sub>], hydrochloric acid [HCl], ethylene [C<sub>2</sub>H<sub>4</sub>], and nitric acid [HNO<sub>3</sub>]) that were available in the US LCI database were used. Life-cycle emission factors of the remaining materials (sodium [Na], sodium amide [NaNH<sub>2</sub>], nitrous oxide [N<sub>2</sub>O], sodium azide [NaN<sub>3</sub>], hydrazoic acid [HN<sub>3</sub>], ethylene [C<sub>2</sub>H<sub>2</sub>], 1,2,3-triazole [C<sub>2</sub>N<sub>3</sub>H<sub>3</sub>]) were calculated using the theoretical approach explained in section 2. These emission factors have been applied to the inputs to calculate the life-cycle emissions for ionic salt and TNT production thereby completing the output side of the inventory (LCI).

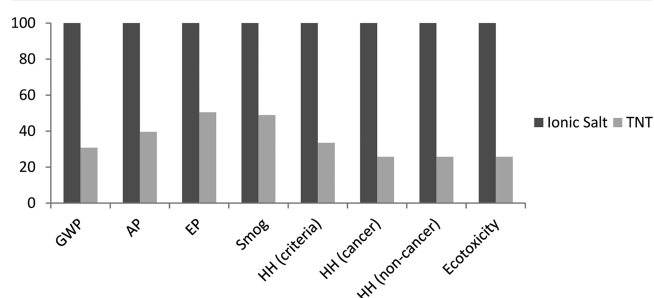
*Life Cycle Impact Assessment.* The life cycle impact assessment methods describe environmental impacts based on characterization factors. These characterization factors are developed by consideration of inherent characteristics of chemicals (for example toxicity) as well as information on fate and transport and possible mode of exposure. The life-cycle impact assessment (LCIA) methodology based on Tools for the Reduction and Assessment of Chemical and other Environmental Impacts (TRACI) developed by the U.S. Environmental Protection Agency was used in this study. This method was considered the most appropriate since it is based on United States data and models. This study considers only midpoint impacts as endpoint impact modeling brings in additional uncertainty to the results and TRACI is primarily a midpoint impact assessment method. Midpoint impact categories quantify the relevant emissions and resources from the life-cycle inventory in terms of common reference substances (e.g., kg CO<sub>2</sub> eq). The impact categories considered are the following: (1) global warming; (2) acidification; (3) eutrophication; (4) smog formation; (5) human health criteria; (6) human health cancer; (7) human health noncancer; and (8) ecotoxicity. Classification and characterization steps of LCA were applied to relate individual elementary flows in the inventory to the impact categories and to identify relevant characterization factors based on the media to which the emissions occur. Normalization was not considered in this study as normalization factors based on U.S. data were not available.

*Sensitivity Analysis.* The main source of uncertainty in this study relates to the conversion factors used for translating theoretical electricity and thermal energy requirement to actual

energy consumed in an industrial plant. A sensitivity analysis is performed to study the effect of varying the conversion factors  $\pm 30\%$ . We examine in detail how sensitive the results are to changes in these conversion factors.

## RESULTS AND DISCUSSION

This section summarizes the main findings from comparing the ionic salt with TNT. The total scores of each environmental impact category for 1,2,3-triazolium nitrate and TNT are shown in Table 1. The impact profiles resulting from production of 1.62 kg of ionic salt and 1 kg of TNT are shown in Figure 3,



**Figure 3.** Comparison of scaled impacts of ionic salt and TNT (functional unit of 1 MJ energy content): GWP (global warming potential), AP (acidification potential), EP (eutrophication potential), HH (human health).

with ionic salt impact set at 100% and TNT displayed as a level relative to the former. Relative comparisons between the ionic salt and TNT (Figure 3) show that in all of the analyzed categories ionic salt had significantly higher environmental/health impact than TNT. With respect to climate change, ionic salt production has roughly three times higher environmental burden than TNT production. In the category of human health, ionic salt is roughly 3, 4, and 4 times more impactful than TNT for criteria, cancer, and noncancer cases, respectively. The environmental burden of IL is higher by approximately 2.5, 2, 2, and 4 times that of TNT for acidification, eutrophication, smog formation, and ecotoxicity, respectively.

The climate change indicator, global warming potential (GWP), is dominated by CO<sub>2</sub> emissions during the life cycle of both IL and TNT production. CO<sub>2</sub> emissions account for 96% of total GWP for both IL and TNT with methane accounting for the remaining 4%. Sulfur dioxide (70% for IL and 58% for TNT) and nitrous oxide (27% for IL and 33% for TNT) emissions dominate acidification indicator while photochemical smog is dominated by nitrogen oxide emissions (90% for both IL and TNT). Eutrophication potential is dominated by nitrogen oxide (98.98% for IL and 96.22% for TNT) emissions. The human health criteria indicator is dominated by sulfur dioxide emissions (93% for IL and 90% for TNT) while human health cancer and noncancer indicators are entirely due to

benzene emissions. The ecotoxicity indicator is also entirely due to benzene emissions.

The results of the cradle to gate life cycle comparison unequivocally shows that energetic ionic salts, such as 1,2,3-triazolium nitrate, have a larger environmental burden than traditional energetic materials such as TNT. This disproves the commonly accepted notion that ionic liquids and ionic salts are green. Though ionic compounds are inherently benign due to their negligible vapor pressure, this fact alone does not make them green. A holistic analysis that includes the inherent properties of the ionic salt, emissions associated with their production, exposure, and end-of-life impacts needs to be considered. This study provides greater insights into the greenness of energetic ionic materials through a more holistic approach.

Closer examination of the results reveal that a majority of the life-cycle environmental burden can be attributed to energy consumption (electricity and natural gas). This is due to the fact that emissions during the energetic material production phase (reaction and separation) dominates other phases such as raw material extraction and transportation. Moreover the environmental footprint of the ionic salts is much larger than TNT due to the fact that steps involved in producing ionic salts and their precursors are much more energy intensive than the steps to produce TNT. This translates into a significant increase in environment and health impacts across all categories. Since most of the emissions in this study can be attributed to electricity and natural gas consumption, using more efficient industrial plants, and/or finding alternate synthesis pathways can result in net energy savings and help offset some of the emissions. Utilization of renewable resources such as solar, wind, and waste biomass to produce electricity can significantly reduce the overall environmental footprint of the production process.

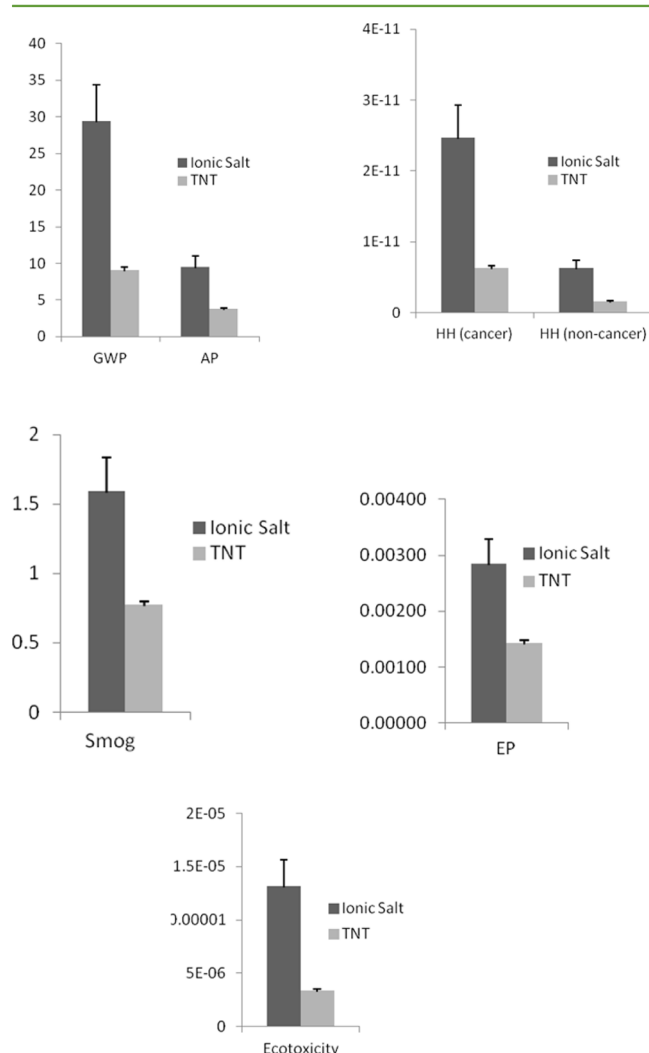
**Uncertainty.** Uncertainties related to conversion factors used for extrapolating theoretical energy calculations to actual energy consumption were addressed via sensitivity analysis. Additional sources of uncertainties are identified as follows: (a) all calculations were based on the life-cycle tree (eqs 1a–7) and it is possible that alternate methods (reactions) exist for producing one or more of the precursors; (b) the reaction yields are based on lab-scale experiments from the literature; (c) we assume majority of the environmental impacts for ionic salt and precursor production processes (i.e., life-cycle tree) can be attributed to the energy intensive reaction and separation steps which could be a source of uncertainty; (d) the calculations in this study are based on the assumption of small-scale batch processes for producing the ionic salt and precursors which could be another source of uncertainty if future manufacturing plants are continuous.

**Sensitivity.** The sensitivity of the LCA results to *theoretical-energy-to-actual-energy conversion factor* is shown in Table 2 and

**Table 2. Sensitivity Analysis**

substance	GWP	AP	EP	smog	HH (cancer)	HH (noncancer)	ecotoxicity
ionic salt (IS)	29.4739	9.4894	0.00285	1.5888	$2.473 \times 10^{-11}$	$6.261 \times 10^{-12}$	$1.32 \times 10^{-5}$
IS (+30%)	34.3751	11.029	0.00328	1.833	$2.93 \times 10^{-11}$	$7.420 \times 10^{-12}$	$1.56 \times 10^{-5}$
IS (−30%)	24.5725	7.9499	0.00241	1.3447	$2.015 \times 10^{-11}$	$5.103 \times 10^{-12}$	$1.07 \times 10^{-5}$
TNT	9.0731	3.7521	0.00144	0.7772	$6.35 \times 10^{-12}$	$1.608 \times 10^{-12}$	$3.38 \times 10^{-6}$
TNT (+30%)	9.48553	3.8905	0.00148	0.7988	$6.616 \times 10^{-12}$	$1.675 \times 10^{-12}$	$3.52 \times 10^{-6}$
TNT (−30%)	8.65707	3.6126	0.00140	0.7554	$6.081 \times 10^{-12}$	$1.540 \times 10^{-12}$	$3.24 \times 10^{-6}$

Figure 4. The conversion factor was varied by  $\pm 30\%$  to study how sensitive the results are to this parameter. The error



**Figure 4.** Sensitivity analysis of the scaled impacts of ionic salt and TNT (functional unit of 1 MJ): GWP (global warming potential), AP (acidification potential), EP (eutrophication potential), HH (human health).

margins indicate that the results are highly robust to changes in this parameter, and all conclusions that were previously arrived at are fully valid.

The proportional size of the error bars indicate that the impacts associated with the ionic salt are more sensitive to this parameter (conversion factor) than for TNT. This is due to the

fact that there are more upstream reactions steps (shown in the life-cycle tree) for ionic salt and hence the conversion factor is applied multiple times (in comparison to TNT). For bigger conversion factors the difference between ionic salt and TNT impacts will be even more than predicted. A comprehensive search of industrial data and a detailed analysis indicates that the considered conversion factors (3.2 and 4.2) fall in the lower end which implies that the LCA results presented here are conservative estimates.

**Scenario Analysis.** In order to investigate the influence of the use of renewable energy on ionic salt production processes, we developed two hypothetical scenarios as follows: (1) In the first scenario cooling energy (electricity) required for all materials needed during ionic salt production (final reaction/separation unit as well as all upstream reaction/separation units) comes from wind (renewable source). (2) In the second scenario wind energy is used only in the last two stages of “triaozle” and “ionic salt” production. The second scenario is more likely and meaningful due to the fact that an ionic liquid production plant is likely to purchase the primary raw materials (acetylene, hydrazoic acid, and nitric acid—upstream processes) from other industries that would likely use electricity from grid. For both scenarios, natural gas is assumed to deliver the required heating energy. In both cases of comparison, it is assumed that fossil energy is completely used for TNT production. The results for the two scenarios are summarized in Tables 3 and 4, respectively. It can be concluded that under scenario one the environmental impact of ionic salt, in most categories, is lower than TNT. However, under scenario two (more realistic) the environmental impact of ionic salt is still significantly higher than TNT. It will be reasonable to assume that under a scenario where only renewable energy is used (in all stages) for both ionic salt and TNT production, the magnitude of environmental impact for both cases will be lowered proportionally; however, the final analysis and conclusions presented in relation to the comparison between them will still hold true (since ionic salt production processes consume significantly more life cycle energy than TNT production processes).

The analysis presented in this study considers only the life-cycle energy consumption. Environmental impacts associated with emissions were not assessed. In order to get a more complete picture, it is necessary to perform a cradle-to-grave life-cycle assessment that will include indirect emissions, direct material emissions (of ionic salt, precursors, etc.) during production phase, as well as end-of-life (after use) impacts of the energetic materials. However, this is not currently possible as the state-of-the-art impact assessment methods, such as TRACI<sup>32</sup> and Eco Indicator,<sup>33</sup> do not contain characterization factors for ionic salts and many of their precursor materials.

**Table 3. Environmental Impact for Scenario 1**

category	units	ionic salt	TNT
global warming	kg CO <sub>2</sub> eq	2.778853	9.073098
acidification	kg H <sup>+</sup> mole eq	0.541855	3.752114
HH criteria	kg PM <sub>10</sub> eq	0.000932	0.007940
eutrophication	kg N eq	0.0003745	0.0014373
smog	kg O <sub>3</sub> eq	0.197913	0.777181
ecotoxicity	CTU-eco	$3.94306 \times 10^{-6}$	$3.3806 \times 10^{-6}$
human health (cancer)	CTU-cancer	$7.40643 \times 10^{-12}$	$6.34994 \times 10^{-12}$
human health (noncancer)	CTU-noncancer	$1.87544 \times 10^{-12}$	$1.60791 \times 10^{-12}$

Table 4. Environmental Impact for Scenario 2

category	units	ionic salt	TNT
global warming	kg CO <sub>2</sub> eq	27.29388	9.0730977
acidification	kg H <sup>+</sup> mole eq	8.758716	3.752114
HH criteria	kg PM <sub>10</sub> eq	0.021851	0.007939
eutrophication	kg N eq	0.00264587	0.00143729
smog	kg O <sub>3</sub> eq	1.475256	0.777181
ecotoxicity	CTU-eco	$1.24115 \times 10^{-5}$	$3.3806 \times 10^{-6}$
human health (cancer)	CTU-cancer	$2.33131 \times 10^{-11}$	$6.34994 \times 10^{-12}$
human health (noncancer)	CTU-noncancer	$5.90329 \times 10^{-12}$	$1.60791 \times 10^{-12}$

Therefore, there is a great need for future research to focus on the fate, transport, and mechanism of damage to human and ecosystem species by ionic salts, ionic liquids, and their precursor materials. This will allow us to develop characterization factors for these compounds and help us investigate the exposure and end-of-life impacts of the emitted material.

## CONCLUSIONS

Cradle-to-gate life-cycle assessment reveals higher environmental impact for energetic ionic salt in comparison to traditional energetic materials. This result contradicts the widely held view that all ionic compounds (liquids and salts) are greener than their molecular counterparts. These results can be attributed to the fact that the series of reaction/separation steps required to produce these energetic salts are energy intensive. These results combined with other findings on the toxicity of ionic salts necessitate more thorough investigation before energetic ionic salts can legitimately be claimed to be more environmentally benign than their molecular counterparts. These results also suggests that different ionic salts may have different environmental impact (depending on the energy intensity of the production processes), and it is important to consider the life cycle of each salt independently without generalizing all ionic salts as green.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation (CAREER Program) under Grant No. 1151182.

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