CHEMICAL ENGINEERING TRANSACTIONS

VOL. 61, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar S Varbanov, Rongxin Su, Hon Loong Lam, Xia Liu, Jiří J Klemeš

ISBN 978-88-95608-51-8; **ISSN** 2283-9216

DOI: 10.3303/CET1761043

Carbon and Nitrogen Footprint Optimisation of Ammonia as an Automotive Fuel

Donna A. Angeles, Kristian Ray Angelo G. Are, Luis F. Razon, Raymond R. Tan*

Chemical Engineering Department, De La Salle University, 2401 Taft Avenue, 0922 Manila, Philippines
raymond.tan@dlsu.edu.ph

The transportation sector is one of the primary contributors to the global CO_2 emissions. Recent research suggests that ammonia is a potential alternative automotive fuel due to its favorable storage properties and the mature infrastructure for its production and distribution. However, there remains the question of whether ammonia can be a sustainable alternative automotive fuel on a life-cycle basis. The energy-intensive production process and the need for a secondary fuel are two major issues with the use of ammonia. A comparative well-to-wheel life cycle assessment of selected ammonia-based fuel cycles is done. Two conventional fossil fuel-based ammonia production processes and two proposed biomass-based processes are considered, namely: steam reforming, partial oxidation, a cyanobacterial (Anabaena) process, and a willow-based (*Salix*) process. The end-use is propulsion of a light-duty internal combustion engine vehicle, and the functional unit is 1 km of distance driven by a such a vehicle. Three types of secondary fuels are considered: gasoline, diesel, and dimethyl ether. Using the carbon and nitrogen footprint as the primary environmental performance indicators, fuzzy life cycle optimization is applied to determine the optimal system configuration. Results show that ammonia produced from the biomass-based process with dimethyl ether as the secondary fuel results in the best well-to-wheel fuel pathway. Sensitivity analysis shows that the end-user vehicle fuel economy has the most significant influence on the optimal solution, which means that concerted efforts to improve ammonia-based fuel cycles must be focused on the end-use phase.

1. Introduction

Ammonia is one of the world's most important commodity chemicals. It is produced primarily via the energy-intensive Haber-Bosch process, although biomass-based processes such as the use cyanobacteria (Razon, 2014a) and willow (Ahlgren et al., 2008) have been proposed. Razon (2014b) discussed the sustainability issues arising from the nitrogen footprint of large-scale ammonia production, which is essential for fertilizer production. Ammonia has also been speculatively identified as a potential automotive fuel, due to its favorable thermodynamic properties and the mature infrastructure for its handling and storage (Zamfirescu and Dincer, 2008). Engine tests have been performed to determine the emission characteristics of ammonia paired with gasoline (Ryu et al., 2014), dimethyl ether (DME) (Gross and Kong, 2013), and diesel (Reiter and Kong, 2011) when used as a fuel in vehicles propelled by internal combustion engines (ICEV). Common issues have been identified in these tests, namely, reduced combustion efficiency (due to the narrow flammability limit, low flame speed, and high combustion temperature of ammonia) and a notable increase in NO_x and NH_3 emissions in the exhaust gas.
Assessment of the sustainability of ammonia-based transportation systems has to be done based on a life cycle perspective. For example, a comparative life cycle assessment (LCA) of selected ammonia production methods has been done previously (Bicer, 2016), using a "cradle to gate" scope (i.e., without consideration of end use). Different environmental issues in LCA are now also known as "footprints" which address specific types of impacts; for example, carbon footprint is used as a metric to quantify climatic impact of a system (Čuček et al., 2012). Despite its broad applicability, LCA has the inherent limitation that it can only be used to analyze a system of predefined configuration. Life cycle optimization (LCO) has been proposed as an extension to identify the environmentally optimal configuration of a process system. The earliest form of LCO made use of a linear programming (LP) formulation (Azapagic and Clift, 1998), which was soon followed by a multi-objective LP

Please cite this article as: Angeles D.A., Are K.R.A.G., Razon L.F., Tan R.R., 2017, Carbon and nitrogen footprint optimisation of ammonia as an automotive fuel, Chemical Engineering Transactions, 61, 271-276 DOI:10.3303/CET1761043

(MOLP) extension (Azapagic and Clift, 1999). A fuzzy LP (FLP) formulation was proposed by Tan et al. (2008) based on a linear algebra computational framework for LCA (Heijungs and Suh, 2002); this approach was later applied to biofuel supply chains (Tan et al., 2009). More recently, LCO has been used for optimizing bioenergy systems (Čuček et al., 2011), shale gas supply chains (Gao and You, 2015) and petrochemical complexes (González Castaño et al., 2015). The combined framework may be extended to include sensitivity analysis as a tool to further support the decision-making.

In this work, the LCO model proposed by Tan et al. (2008) is applied to the case of ammonia automotive fuel, using carbon footprint and nitrogen footprint as environmental indicators to evaluate selected well-to-wheel fuel cycles. The succeeding sections are as follows. Section 2 covers the system description and problem statement, followed by discussion of the model formulation in Section 3, the results in Section 4, and lastly, conclusions in Section 5.

2. System description and problem statement

In this study, two commercial, fossil fuel-based processes are considered, namely, steam reforming (SMRF) and partial oxidation (PROX). The steam reforming process uses natural gas as feedstock and consists of the following steps: desulfurization, primary and secondary reforming, CO shift, CO_2 removal, and methanation. The partial oxidation uses heavy oil as feedstock, and includes the following steps: oxidation, sulfur removal, CO-shift, CO_2 removal, and nitrogen wash. Both of these processes are highly energy-intensive due to the need for fossil fuel inputs. In addition, two biomass-based processes are included as options, namely, the cyanobacterial process (ANAB) and the willow-based process (SALI). The cyanobacterial process was based from the work of Razon (2014) and involves the cultivation of Anabaena in raceway ponds, biogas production, separation into biogas and digestate, and conversion from digestate to ammonia. The data for willow-based process was derived from the works of Ahlgren et al. (2008). In their work, ammonium nitrate is produced from Salix (short rotation willow coppice) and cereal straw. The data from Salix was chosen as representative as it has the lower impacts. The process diagram by Ahlgren et al. (2008) was modified so that the final product is liquid ammonia instead of ammonium nitrate. The ammonium nitrate production and nitric acid production processes were removed, and replaced with compression or liquefaction of gaseous ammonia. The whole process may be summarized into two major processes: biomass production (consisting of planting, managing, and harvesting) and ammonia production (consisting of gasification, gas cleaning, H_2 separation, and ammonia production). Both biomass-based systems are significantly less fossil energy-intensive than the conventional processes, since much of the energy input comes in the form of solar energy absorbed during biomass growth. Regardless of the type of production process, the ammonia produced is delivered and distributed via conventional freight transport (APMT); this is an important assumption since the mode of transport in the ammonia supply chain determines part of its carbon footprint.

Since pure ammonia is not suitable as fuel for current ICEVs, three types of conventional fuels are paired with ammonia in this study: gasoline, diesel, and DME. The production of gasoline (GAPR) and diesel (DIPR) include the following processes: extraction of feedstock (crude oil), feedstock transport, and refining. The DME production chain includes feedstock extraction (natural gas), steam production, and DME synthesis from CO and H_2O. Similarly, the fuels are delivered and distributed via freight transport that relies on diesel fuel. Diesel transport is labeled as DITR, dimethyl ether transport is labeled as DMTR and gasoline transport is labeled as GATR. The fuels are used in conjunction with ammonia for light-duty ICEVs, whose emission characteristics are based on the experimental results of Reiter and Kong (2011) for ammonia-diesel (DIVO), Gross and Kong (2013) for ammonia-DME (DMVO), and Ryu et al. (2014) for ammonia-gasoline (GAVO). The proportions of fuels are based on the conditions of highest engine performance reported in these works. The emissions that were considered in the analysis were CO_2, CH_4, N_2O, NO_x, and NH_3, and all the fossil energy inputs are expressed in terms of primary energy (PE). Note that the latter excludes solar energy inputs for biomass growth.

Given these system components, the problem is to determine the optimal system configuration that minimizes the carbon and nitrogen footprints per functional unit (i.e., per unit distance travelled by a representative end-user ICEV).

3. Model formulation

The LCO model is formulated as follows:

$$\max \lambda \tag{1}$$

subject to:

$$As = f \tag{2}$$

$$Bs = g \tag{3}$$

$$Qg = h \tag{4}$$

$$(h - h^U) \leq \lambda(h^L - h^U) \tag{5}$$

where λ is the fuzzy dimensionless degree of goal satisfaction, A is the technology matrix, f is the functional unit vector, s is the scaling vector, B is the intervention matrix, g is the inventory vector, h is the impact vector, and Q is the characterization matrix. The vectors h^L and h^U signify the lower and upper limits of h. The lower limit may be set at zero for an idealized system with no footprint. The objective function seeks to maximize λ as given by Eq(1); thus, the model optimizes the degree to which fuzzy environmental impact limits are met on a dimensionless scale ranging from 0 to 1. Energy and material balances in the supply chain within the system are defined by Eq(2), while mass balances for emissions are given by Eq(3). The flows of emissions are translated to corresponding footprints using Eq(4). Finally, the fuzzy limits for the footprints are defined by Eq(5). Note that the value λ of approaches 1 as the values in **h** approach those of corresponding elements in $\mathbf{h}^L$. A more detailed description of this formulation can be found in Tan et al. (2008). Note that the model is linear, so that no computational issues arise in seeking a global optimum. In this work, the model is implemented using the optimization software LINGO 14.0.

4. Case study and results

As described in Section 2, the system is comprised on four ammonia production options and three vehicle end-use options. The functional unit is 1 km distance driven by a representative light-duty ICEV, which is a common reference value used in the LCA of automotive fuel pathways. The input-output data (matrices **A** and **B**) of commodities (i.e., intermediate and products) and emissions are given in Table 1.

Table 1: Input and output flows of commodities and emissions.

Process	Outflows	Inflows	Emissions	Reference
ANAB	1 kg Ammonia	5.1 MJ PE	0.06 kg CO_2	Razon (2014)
SALI	1 kg Ammonia	1.1 MJ PE	0.08 kg CO_2; 0.003 kg CH_4;0.001 kg N_2O; 0.0009 kg NO_x; 0.0006 kg NH_3	Ahlgren et al. (2008)
SMRF	1 kg Ammonia	11.09 MJ PE	1.59 kg CO_2; 0.00004 kg CH_4; 0.002 kg N_2O; 0.0007 kg NO_x	Ahlgren et al. (2008)
PROX	1 kg Ammonia	48.8 MJ PE	2.9 kg CO_2	Ecoinvent (2016)
APMT	1 kg Ammonia	0.185 MJ PE	0.0025 kg CO_2	Ecoinvent (2016)
DIPR	25.2 kg Diesel	188.5 MJ PE	9.1 kg CO_2; 0.01 kg CH_4; 0.0001 kg N_2O; 0.01 kg NO_x	Wang (2001)
DMPR	36.7 kg DME	1937.8 MJ PE	98.6 kg CO_2; 0.01 kg CH_4; 0.001 kg N_2O; 0.09 kg NO_x	Wang (2001)
GAPR	24.2 kg Gasoline	252.3 MJ PE	13.0 kg CO_2; 0.02 kg CH_4; 0.0002 kg N_2O; 0.02 kg NO_x	Wang (2001)
DITR	25.2 kg Diesel	25.2 kg Diesel	1.37 kg CO_2; 0.002 kg CH_4; 0.00002 kg N_2O; 0.006 kg NO_x	Wang (2001)
DMTR	36.7 kg DME	36.7 kg DME	2.54 kg CO_2; 0.003 kg CH_4; 0.00002 kg N_2O; 0.006 kg NO_x	Wang (2001)
GATR	24.2 kg Gasoline	24.2 kg Gasoline	1.5 kg CO_2; 0.002 kg CH_4; 0.00002 kg N_2O; 0.006 kg NO_x	Wang (2001)
DIVO	1.6 km	0.05 kg NH_3 0.01 kg Diesel	0.1 kg CO_2; 0.001 kg NO_x; 0.000007 kg NH_3	Reiter and Kong (2011)
DMVO	1.6 km	0.03 kg NH_3 0.02 kg DME	0.003 kg CO_2; 0.0005 kg NO_x; 0.0005 kg NH_3	Gross and Kong (2013)
GAVO	1.6 km	0.06 kg NH_3 0.02 kg Gasoline	0.2 kg CO_2; 0.0002 kg CH_4; 0.00001; kg N_2O; 0.0005 kg NO_x; 0.005 kg NH_3	Ryu et al. (2014)

The life cycle system has excess degrees of freedom in the technology matrix **A** due to the presence of alternative technological options. It is necessary for the model to balance the carbon footprint and nitrogen footprints as potentially conflicting environmental objectives. The mass ratios of fuels in the vehicle operation phase is based on the most favorable operating condition of the vehicle i.e. conditions with highest engine performance and/or highest energy production per mass of fuel based from the experimental result of Reiter and Kong (2011), later extended by Gross and Kong (2013), and recently by Ryu et al. (2014). The scope of this work excludes the infrastructure and ammonia fugitive emissions (Bicer et al., 2016) in the ammonia production phase. Such considerations may result in similar nitrogen footprints for all options regardless of the ammonia production process. Table 2 shows the values in the characterization matrix **Q**.

Table 2: LCO model characterization factors.

Footprint	Environmental Emissions				
	CO_2	CH_4	N_2O	NO_x	NH_3
Carbon	1	25	298	0	0
Nitrogen	0	0	0.64	0.37	0.82

Solving the model gives a global index of satisfaction of $\lambda = 0.79$. This result indicates that *Salix*-based ammonia paired with DME offers the best compromise in terms of carbon and nitrogen footprint reduction. The total flows of primary energy and emissions per functional unit are summarized in Table 3. For this optimal pathway, the carbon footprint is determined to be 27.13 g CO_2 equivalent per km while the nitrogen footprint is 0.49 g reactive nitrogen per km. Sensitivity analysis suggests that vehicle fuel economy is a more significant factor than the efficiency of upstream processes that comprise the ammonia production system. This result means that it is essential for more data on engine tests to be collected, especially under varying load conditions. Acquisition of such data can improve the precision of the results of the LCO in the future. In addition, improvements in the efficiency of upstream production chain (e.g., through the application of Process Integration methodology), will also help reduce the carbon and nitrogen footprints of ammonia-based systems, which has been documented for the case of fossil fuel-based processes (Ruddock et al., 2003), while similar opportunities exist to apply Process Integration methodology to optimize biomass-based ammonia production.

Table 3: Optimal emission and resource flows per functional unit.

Resource or pollutant	Total flowrate per functional unit
Primary Energy	0.4 MJ/km
CO_2	14.72 g/km
CH_4	0.07 g/km
N_2O	0.04 g/km
NO_x	0.40 g/km
NH_3	0.38 g/km

Figure 1 shows the carbon footprint of selected fuel cycles, where BASE represents the option when only pure diesel, DME, or gasoline is used during the vehicle operation phase. The use of ammonia-DME in the vehicle operation stage results in the lowest carbon footprint, followed by ammonia-diesel and ammonia-gasoline fuel, regardless of the choice of ammonia production. The addition of ammonia reduces the amount of hydrocarbon fuel needed to achieve the same mechanical power output; CO_2 emissions are reduced in the exhaust gas. It also offers the most notable reduction in carbon footprint when combined with DME. Figure 1 also shows that Salix process for ammonia production offers the lowest carbon footprint, followed in ascending order by the Anabaena process, steam reforming and partial oxidation. The results show that, in terms of carbon footprint reduction, a shift to biomass-based ammonia production is preferable, while fossil fuel-based ammonia gives little benefit. However, the use of ammonia also results in an increase in nitrogen footprint for all fuel mixtures relative to the BASE case, as shown in Figure 2. In particular, the use of ammonia-gasoline mixture had the highest nitrogen footprint, which may be attributed to high levels of NO_x produced in engine combustion chambers, as well as the unburned ammonia, or ammonia slip, detected in the exhaust gases after combustion (Ryu et al., 2014). The synergistic effect of low peak combustion temperature achieved in a spark-ignition engine and unfavorable properties of ammonia lead to considerably higher nitrogen footprint in ammonia-gasoline mixtures compared to the other blends. These results indicate that there are significant unfavorable effects in the use of ammonia blends in engines optimized to run on conventional fuels. Thus, it will also be necessary to determine how engines can be customized or retrofitted to achieve more favorable combustion conditions for ammonia blends.

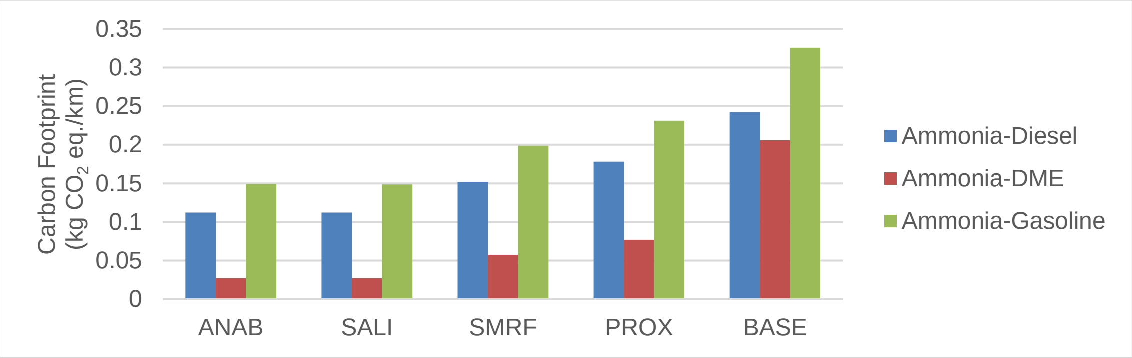

Figure 1: Carbon footprint of selected ammonia-based fuel cycles.

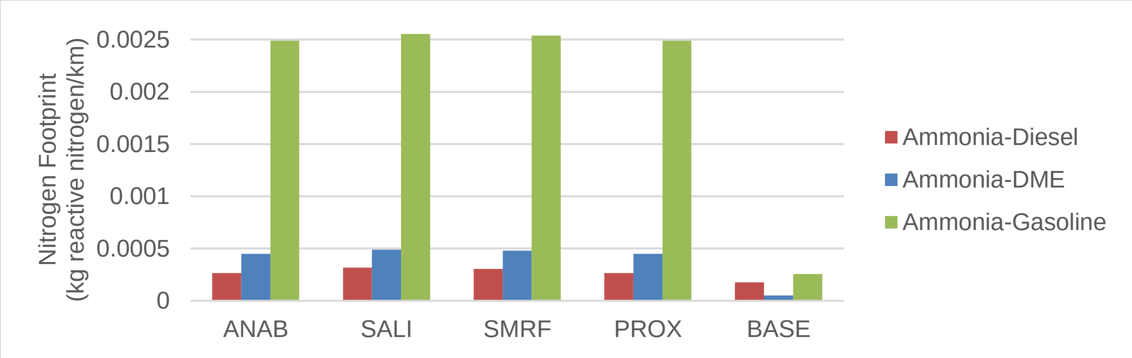

Figure 2: Nitrogen footprint of selected ammonia-based fuel cycles.

5. Conclusions

In this work, an LCO model formulated as an FLP was developed and solved to optimize the carbon and nitrogen footprints of ammonia used as an automotive fuel. The model was calibrated using data from experimental literature, as well as existing LCA databases and models. The optimal pathway identified involves production of ammonia using the Salix process, coupled with its utilization in conjunction with DME. Future work can focus on extensive uncertainty analysis due to the limited availability of data on the performance of ammonia-fueled engines. Such analysis can be done using a design of experiment (DOE) strategy, which has been used in the past for LCA (Rivera and Sutherland, 2014) and for optimization problems (Tan et al., 2015). In addition, a more detailed assessment using a life cycle sustainability assessment (LCSA) framework that also covers economic and social dimensions will be necessary to firmly establish if use of ammonia as an automotive fuel can be a truly viable option.

Acknowledgments

The authors wish to acknowledge financial support of the Philippines' Department of Science and Technology (DOST) via the Engineering Research for Development and Technology (ERDT) scholarship program.

References

Ahlgren S., Baky A., Bernesson S., Nordberg A., Noren O., Hansson, P.A., 2008, Ammonium nitrate fertiliser production based on biomass – environmental effects from a life cycle perspective, Bioresource Technology, 99, 8034-8041.

Azapagic, A., Clift, R., 1998, Linear programming as a tool in life cycle assessment, International Journal of Life Cycle Assessment, 3, 305-316.

Azapagic, A., Clift, R., 1999, Life cycle assessment and multiobjective optimisation, Journal of Cleaner Production, 7, 135-143.

Bicer, Y., Dincer, I., Zamfirescu, C., Vezina, G., Raso, F., 2016, Comparative life cycle assessment of various ammonia production methods, Journal of Cleaner Production, 135, 1379-1395.

Čuček, L., Klemeš, J.J., Varbanov, P.S., Kravanja, Z., 2011, Life cycle assessment and multi-criteria optimization of regional biomass and bioenergy supply chains, Chemical Engineering Transactions, 25, 575-800.

Čuček, L., Klemeš, J.J., Kravanja, Z., 2012, A review of footprint analysis tools for monitoring impacts on sustainability, Journal of Cleaner Production, 111, 140-144.

Ecoinvent, 2013, <www.ecoinvent.org> accessed 1.10.2016.

Gao, J., You, F., 2015, Sustainable design and operation of shale gas supply chain networks with life cycle economic and environmental optimisation, Chemical Engineering Transactions, 45, 493-498.

González Castaño, A., Bandoni, J.A., Díaz, M.S., 2015, Life cycle optimization for sustainable operations in a petrochemical complex, Chemical Engineering Transactions, 43, 1441-1446.

Gross, C.W., Kong, S.C., 2013, Performance characteristics of a compression-ignition engine using direct injection ammonia-DME mixtures, Fuel, 103, 1069-1079.

Heijungs, R., Suh, S., 2002, The Computational Structure of Life Cycle Assessment, Kluwer, Dordrecht, Netherlands, 243 ps. ISBN: 978-90-481-6041-9.

Razon, L. F., 2014a, Life cycle analysis of an alternative to Haber-Bosch process: non-renewable energy usage and global warming potential of liquid ammonia from cyanobacteria, Environmental Progress and Sustainable Energy, 33, 618-624.

Razon, L. F., 2014b, Is nitrogen fixation (once again) “vital to the progress of civilized humanity”?, Clean Technologies and Environmental Policy, 17, 301-307.

Reiter, A., Kong, S.C., 2011, Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel, Fuel, 90, 87-97.

Rivera, J.L., Sutherland, J.W., 2014, A design of experiments (DOE) approach to data uncertainty in LCA: Application to nanotechnology evaluation, Clean Technologies and Environmental Policy, 17, 1585-1595.

Ruddock, J., Short, T.D., Brudenell, K., 2003, Energy integration in ammonia production, Sustainable World, 7, 267-276.

Ryu, K., Zacharakis-Jutz, G., Kong, S.C., 2014, Effects of gaseous ammonia direct injection on performance characteristics of a spark-ignition engine, Applied Energy, 116, 206-215.

Tan, R.R., Culaba, A.B., Aviso, K.B., 2008, A fuzzy linear programming extension of the general matrix-based life cycle model, Journal of Cleaner Production, 16, 1358-1367.

Tan, R.R., Ballacillo, J.-A., Aviso, K.B., Culaba, A.B., 2009, A fuzzy multiple-objective approach to the optimization of bioenergy system footprints, Chemical Engineering Research and Design, 87, 1162-1170.

Tan, R.R., Aviso, K.B., Uy, O.M., 2015, Comprehensive sensitivity analysis in NLP models in PSE applications using space-filling DOE Strategy, Chemical Engineering Transactions, 45, 523-528.

Wang, M.Q., 2001, Development and use of GREET 1.6 fuel-cycle model for transportation fuels and vehicle technologies, Technical Report ANL/ESD/TM-163, Center for Transportation Research, Energy Systems Division, Argonne National Laboratory, Argonne, Illinois, USA.

Zamfirescu, C., Dincer, I., 2008, Using ammonia as sustainable fuel, Journal of Power Sources, 185, 459-465.