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Optimization of Ammonia Co-Firing Networks

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Ammonia produced using renewable inputs, or green ammonia, is a promising fuel for deep decarbonization in the industrial, transportation, and power generation sectors. Like green hydrogen, it is a carbon-neutral energy carrier without the associated challenges in handling and storage. The use of pure ammonia in combustion systems entails extensive retrofits or investment in new, dedicated systems due to significant changes in flame speed and air-fuel ratio compared to natural gas. On the other hand, ammonia can be blended with natural gas to achieve partial decarbonization with minimal modifications to combustion systems. The blending limits depend on the specific characteristics of the equipment used as well as the risk appetite of firms to accept some degree of performance loss. In this work, a mathematical programming model is developed to optimize ammonia co-firing networks consisting of ammonia production facilities acting as sources, and ammonia-using plants acting as sinks. Each source has a specified capacity and carbon footprint per unit of product; each sink has a specified upper limit on ammonia demand based on its self-defined blending limit. The model is formulated to allocate the ammonia supply to minimize aggregate carbon emissions. Two representative case studies are used to illustrate the model's capabilities, with system-wide substitution rates of 17.2 % and 15.1 % being achieved.

1. Introduction

There is an urgent need for deep decarbonization leading to net zero emissions by the middle of this century. Eliminating greenhouse gas (GHG) emissions in the coming decades will be necessary to ensure that global warming is kept at a manageable level (IPCC, 2022). Drastic decarbonization can only be achieved by combining multiple approaches including energy efficiency improvement, replacement of fossil energy with renewables, and sequestration of CO_2 from point sources or directly from the atmosphere (Gailani et al., 2024). Energy efficiency enhancement through Process Integration (PI) is a proven strategy, but the extent of decarbonization is subject to thermodynamic limits (Klemeš, 2023). Deeper process heat decarbonization is possible through electrification (coupled with the use of electricity from renewables) or using carbon-free fuels (Martin, 2023). Similar decarbonization options exist for sectors whose emissions are inherently hard to abate, such as aviation (Su-ungkavatin et al., 2023) or maritime transport (Wang et al., 2023). Each of the available options has drawbacks that hinder large-scale deployment. Examples of technical barriers include transport and storage challenges for hydrogen and storage issues for electricity.

Ammonia is a promising alternative to hydrogen as a fuel for deep decarbonization. It can be considered as a chemical hydrogen carrier. In addition to physical properties that are conducive to relatively easy handling compared to hydrogen, there is extensive experience in transporting and storing ammonia in large quantities (Chehade and Dincer, 2021). This industrial gas is now mostly produced from hydrogen and nitrogen using the energy-intensive Haber-Bosch process, but there are more sustainable alternative production pathways at various stages of technological maturity (Razon, 2018). Ojelade et al. (2023) surveyed these technologies in their recent review article. Electrification can decarbonize ammonia production if an abundant supply of renewables is present (McPherson and Zhang, 2020). Green hydrogen produced via electrolysis can be used to produce green ammonia, as well as other electro-fuels (Nemmour et al., 2023). Alternatively, conventional

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processes can be retrofitted for carbon capture and storage (CCS) to produce so-called blue ammonia with a relatively low carbon footprint (Al-Shamari et al., 2023).

In addition to the range of technologies available to produce sustainable ammonia, there are also alternative options for its end use, either directly as fuel or indirectly via the release of its hydrogen content (Ishaq and Crawford, 2024). One pathway is direct combustion of ammonia to supply high-temperature process heat (Valera-Medina et al., 2024) or to generate electricity in thermal power plants (Aziz et al., 2023). The use of ammonia in combustion systems will require dedicated designs to account for its properties such as a different air-fuel ratio and low flame speed compared to methane. Alternatively, gas turbines in peaking or combined cycle power plants can run on mixtures of ammonia and natural gas (NG) for incremental decarbonization (Pashchenko, 2024). Such co-firing schemes do not need extensive combustor modifications provided that ammonia blending is limited to prevent excessive changes in the flame characteristics of the fuel mixture. However, substantial reductions in life-cycle GHG emissions can only be achieved with decarbonized ammonia production, and even then, there may be adverse impacts from non-GHG air emissions (Razon and Valera-Medina et al., 2021). The option of co-firing ammonia in existing power plants presents the possibility of a substantial reduction in the carbon footprint of electricity in countries or regions that still rely heavily on NG as a power sector fuel. However, doing so on a large scale will present logistical challenges in maximizing the climate benefits of ammonia use, particularly if supply is limited. Although supply chain models have already been developed for ammonia logistics (Prause et al., 2022), no optimization models have yet been developed specifically for ammonia co-firing applications.

This research gap is addressed in this paper through the development of a linear programming (LP) model for optimizing the allocation of fuel ammonia from different sources (ammonia producers) to different sinks (ammonia consumers). The model assumes that ammonia is used to partially displace NG, with a unique blending limit imposed by each user. It uses a PI-based source-sink matching framework which has already proven to be effective for applications involving co-firing of biomass and coal (Aviso et al., 2020). The rest of this paper is organized as follows. Section 2 gives the formal problem statement. Section 3 describes the model formulation. Sections 4 and 5 demonstrate the model on test cases. Section 6 presents the sensitivity analysis. Finally, Section 7 gives the conclusions and discusses future research directions.

2. Problem statement

The formal problem is as follows. Given:

- A set of ammonia sources (producers), each characterized by annual capacity, G_i, and carbon footprint, CG_i;
- A set of ammonia sinks (NG-fired power plants), each characterized by a maximum annual demand, D_j;

It is also assumed that:

- NG is characterized by its carbon footprint, CF;
- The maximum annual demand of each power plant is based on its capacity, thermal efficiency (η_j), and ammonia blending limit (L_j);
- The ammonia blending limit of each power plant is defined by the physical limitations of its gas turbines and the risk appetite of its owner;
- The co-firing of ammonia within the blending limit has a negligible effect on the thermal efficiency of each power plant;

The superstructure for this problem is illustrated in Figure 1. The problem is to determine the allocation of ammonia from the sources to the sinks to minimize the system's total carbon footprint via displacement of NG.

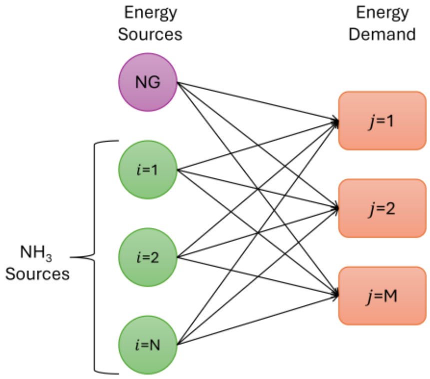

Figure 1: Superstructure of the proposed problem

3. Model formulation

The objective of the optimization model is to minimize the total carbon footprint generated by the system (Eq(1)), where f_j is the flowrate of NG supplied to sink j, CF is the carbon footprint of NG, x_{ij} is the flowrate of ammonia supplied from source i to sink j, and CG_i is the carbon footprint of ammonia from source i. It is assumed that the system operates at 8,000 h/y. The carbon footprint of both NG and ammonia includes upstream emissions from the fuel supply chain including transport; however, variations among source-sink pairs are assumed to be negligible. Each source is limited by its production capacity, G_i (Eq(2)). The fuel requirement of each sink j (e_j) can be satisfied with NG and ammonia (Eq(3)) provided that the ammonia blending limit (L_j) is not exceeded (Eq(4)). The fuel requirement of each sink is a function of its power output (D_j) and thermal efficiency (η_j), as indicated in Eq(5).

$$\min\left(\sum_j f_j CF + \sum_i \sum_j x_{ij} CG_i\right) \times 8{,}000 \tag{1}$$

$$\sum_j x_{ij} \leq G_i \qquad \forall\, i \tag{2}$$

$$f_j + \sum_i x_{ij} = e_j \qquad \forall\, j \tag{3}$$

$$\sum_i x_{ij} \leq L_j e_j \qquad \forall\, j \tag{4}$$

$$e_j = \frac{D_j}{\eta_j} \qquad \forall\, j \tag{5}$$

This LP model can be readily implemented and solved to global optimality using different optimization software. It is applied in the succeeding case studies using Microsoft Excel Solver.

4. Case study 1

Case study 1 considers hypothetical data consisting of 1 ammonia source and 4 power plant sinks. The thermal efficiency is assumed to be 50 % for all sinks, which is typical for NG combined cycle (NGCC) plants, and the blending limit for all plants is set at 20 %. The latter is a conservative limit that prevents excessive changes in flame characteristics in minimally modified gas turbines (Pashchenko, 2024). The limiting data for the sources and sinks are presented in Table 1. The flowrates of NG and ammonia are given in terms of their chemical energy value. Note that the subscript “f” refers to the fuel thermal energy, while the subscript “e” refers to the electrical energy produced.

Solving Eq(1) subject to the constraints outlined in Eq(2) to Eq(5), the optimal allocation of fossil and ammonia is shown in Table 2. The optimal solution has a total carbon footprint of 10.65 Mt CO_{2eq}./y. All the available ammonia is used, and the NG requirement is reduced by 17.2 % to 4,800 MW_f.

Table 1: Limiting data for case study 1

Source	Capacity, G_i (MW_f)	Footprint (kg-CO_{2eq}/kWh_f)	Sink	Electricity output, D_j (MW_e)	Fuel demand, e_j (MW_f)
NG	Unlimited	0.27	D1	1,000	2,000
S1 (NH_3)	1,000	0.035	D2	600	1,200
			D3	500	1,000
			D4	800	1,600

Table 2: Allocation of fuel to sinks, in MW_f for case study 1

Source	D1	D2	D3	D4	Total
NG	1,760	960	800	1280	4,800
S1 (NH_3)	240	240	200	320	1,000
Total	2,000	1,200	1,000	1,600	

5. Case study 2

Case study 2 considers 2 sources of ammonia and 7 power-generating sinks. In this case, there are variations in the thermal efficiencies and ammonia blending limits of the sinks. Different blending limits reflect differences in company policy and risk appetite. The limiting data for the sources and sinks are summarized in Table 3. Solving the model leads to the optimal allocation of fossil and ammonia shown in Table 4. The annual total carbon footprint of the optimized system is 17.43 Mt CO_{2eq}. The total NG requirement of the system is reduced by 15.1 % to 7,891 MW_f, while the total ammonia demand matches the supply limit of 1,400 MW_f. Plants D1 and D5 continue to run on just NG, while all others except for D7 obtain ammonia from only one source. However, alternative optima may also exist for this problem.

Table 3: Limiting data for case study 2

Source	Capacity, G_i) (MW_f)	Footprint (kg-CO_{2eq}/kWh_f)	Sink	Ammonia blending limit, L_j (%)	Efficiency (%)	Electricity output, D_j (MW_e)	Fuel demand, e_j (MW_f)
NG	Unlimited	0.27	D1	20	48	800	1,667
S1 (NH_3)	1000	0.04	D2	25	50	500	1,000
S2 (NH_3)	400	0.02	D3	12	45	400	889
			D4	24	50	1,000	2,000
			D5	15	55	1,000	1,818
			D6	20	48	600	1,250
			D7	22	45	300	6,67

Table 4: Allocation of fuel to sinks, in MW_f for case study 2

Source	D1	D2	D3	D4	D5	D6	D7	Total
NG	1,667	500	866	1,520	1,818	1,000	520	7,890
S1 (NH_3)	0	500	0	480	0	0	20	1,000
S2 (NH_3)	0	0	23	0	0	250	127	400
Total	1,667	1,000	889	2,000	1,818	1,250	667	

6. Sensitivity analysis

Sensitivity analysis is performed by analyzing the shadow prices. Each shadow price gives the change in the optimal objective function value per unit change of the right-hand side of the constraint. Its value is zero for non-binding constraints.

Tables 5 and 6 show the constraint shadow prices for case studies 1 and 2. As expected, increasing the supply of ammonia would decrease the total carbon footprint (–0.00188 Mt CO_{2eq} for every MW_f increase in supply) for case study 1. For case study 2, the same trend is observed, with both supplies having almost the same impact on the objective value (–0.00184 and –0.002 Mt CO_{2eq} for every MW_f increase in supply). On the other hand, increasing the demand for any of the sinks will result in a higher total carbon footprint, with each demand having the same impact on the objective value (0.00216 Mt CO_{2eq} for every MW_f increase in demand) for both cases.

The sensitivity of the solution to the fuel blending limits can also be investigated by isolating L_j on the right-hand side of the constraint. Because these blending limits are determined by each company's discretion based on the perceived technical risks of using ammonia, in practice, the constraints will be flexible. Sensitivity analysis will allow assessment of the trade-off between system carbon footprint and the risk tolerance of the power plant owners. In both cases solved here, the blending limits are non-binding, as reflected in the shadow price values in the last columns of Tables 5 and 6.

Table 5: Shadow prices for each constraint in case study 1

Constraint	Current value (MW_f)	Shadow price (Mt CO_{2eq}/MW)	Constraint	Current value (%)	Shadow price (Mt CO_{2eq})
Energy supply			NH_3 blending limit		
S1 (NH_3)	1,000	−0.00188	D1	20	0
Energy demand			D2	20	0
D1	2,000	0.00216	D3	20	0
D2	1,200	0.00216	D4	20	0
D3	1,000	0.00216			
D4	1,600	0.00216			

Table 6: Shadow prices for each constraint in case study 2

Constraint	Current value (MW_f)	Shadow price (Mt CO_{2eq}/MW)	Constraint	Current value (%)	Shadow price (Mt CO_{2eq})
Energy supply			NH_3 blending limit		
S1 (NH_3)	1,000	−0.00184	D1	20	0
S2 (NH_3)	400	−0.002	D2	25	0
Energy demand			D3	12	0
D1	1,667	0.00216	D4	24	0
D2	1,000	0.00216	D5	15	0
D3	889	0.00216	D6	20	0
D4	2,000	0.00216	D7	22	0
D5	1,818	0.00216			
D6	1,250	0.00216			
D7	667	0.00216			

7. Conclusions

An LP model for optimizing ammonia co-firing networks was developed in this work. The model allocates ammonia from different producers, each with a unique carbon footprint, to a set of NG-fired power plants, each with a unique fuel blending limit. The allocation determined by the model minimizes the system's carbon footprint by maximizing the displacement of NG with ammonia. The LP model is demonstrated in two illustrative case studies where 17.2 % and 15.1 % substitution rates are achieved. The results show how ammonia allocation in any given system can be computed to give the most carbon footprint reduction. The model allows the practical optimization of an interim grid decarbonization solution for countries and regions that remain reliant on NG; this framework can also be applied to other industrial sectors that use NG for process heat. Optimizing the allocation of ammonia for decarbonization benefits will be critical if the supply is limited.

Future work can focus on developing model extensions that take topological constraints, parametric uncertainties, and temporal variations into account. The effect of co-firing on thermal efficiency at higher blending ratios should also be considered. These future extensions will result in non-LP formulations. Multi-objective mathematical programs should also be developed to consider conflicting goals encountered in practice, such as the risks posed by potential ammonia leakage.

Nomenclature

TCF – Total carbon footprint

Parameter

η_j – efficiency of sink j

CF – carbon footprint of fossil fuel, kg-CO_{2eq}/kWh_f

CG_i – carbon footprint of ammonia, kg-CO_{2eq}/kWh_f

D_j – energy demand of sink j as electricity, MW_e

L_j – blending limit of sink j, %

Decision variables

e_j – energy demand of sink j, MW_f

f_j – fossil fuel used in sink j, MW_f

x_{ij} – ammonia from source i to sink j, MW_f

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