



Determination of the oxidative degradation of ethanolamines

Benedetta A. De Liso , Matteo Curcio, Gianmaria Pio , Valerio Cozzani, Ernesto Salzano

LISES – Laboratory of Industrial Safety and Environmental Sustainability, Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, Italy

ARTICLE INFO

Keywords:

Burning rate
Cone calorimeter
Amine
Ethanolamines
Ignition temperature
Pool fire

ABSTRACT

Although pure ethanolamines are hazardous substances widely used in chemical processes (e.g., gas sweetening and pretreatment agents), a dedicated assessment of their fire and degradation properties is missing. Within this scope, an experimental analysis was carried out by using a cone calorimeter to quantify the burning characteristics of the ethanolamines most widely used: monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyl diethanolamine (MDEA). The effects of an external heat flux on ignition temperature, maximum mass burning rate, mass loss rate, heat release rate, and exhaust gas composition of liquid samples were observed. The collected data were employed for the development and quantification of an apparent kinetic rate. The resulting rates were validated against empirical data from the literature, showing excellent agreement. Besides, the radical reactions most relevant for the activation of the investigated amines were identified. The experimental overall reaction rates were compared with theoretically based kinetics of the identified reactions to identify the rate-determining step in the process. The results indicate that the hydrogen abstraction from the nitrogen site by HO_2 can be considered as the rate-determining step for the MEA and DEA cases, and the same agent is ruling the activation of TEA from a carbon site, highlighting the role of low-temperature chemistry in the ignitability of the amines. These observations are useful for the accurate modelling and design of chemical processes involving ethanolamines, for the analysis of prevention and mitigation, and for the evaluation of pool fire likelihood and consequence assessment.

Nomenclature

Symbol	Description	Unit
A	Surface area of the liquid sample exposed to combustion	m^2
b	Instrument constant used in the oxygen consumption calculation	–
C	Calibration factor of the cone calorimeter exhaust system	$\text{kg K}^{0.5}/(\text{atm}^{0.5} \text{ s})$
δ	Flame thickness estimated through the one-dimensional kinetic approach	m
$\Delta h_c/r$	Heat released per unit mass of oxygen consumed	MJ/kg
$\Delta H_{r,i}$	Heat of reaction for the overall oxidation reaction, where i identifies the assumed nitrogen-containing product	MJ/kg
ΔP	Pressure difference across the cone calorimeter exhaust duct	Pa
dT/dt	Temperature rate	K/s
Ea	Activation energy of the considered reaction pathway	kJ/mol
EHC	Effective heat of combustion	MJ/kg
HRR	Heat release rate	kW/m^2

(continued on next column)

(continued)

k_0	Pre-exponential factor of the modified Arrhenius equation	–
MLR	Mass loss rate	g/s
M_i	Molecular weight of the i-species	g/mol
n	Temperature exponent of the modified Arrhenius equation	–
r_a	Apparent overall reaction rate of ethanolamine oxidation	$\text{kmol}/(\text{m}^3 \text{ s})$
$r_{a,\text{Cone}}$	Apparent reaction rate estimated from cone calorimeter experimental data	$\text{kmol}/(\text{m}^3 \text{ s})$
$r_{a,\text{Lit}}$	Apparent reaction rate derived from kinetic parameters available in the literature	$\text{kmol}/(\text{m}^3 \text{ s})$
$r_{a,\text{Th}}$	Apparent reaction rate estimated from theoretical elementary reaction kinetics	$\text{kmol}/(\text{m}^3 \text{ s})$
R	Universal gas constant	$\text{J}/(\text{mol K})$
S_u	Laminar burning velocity	m/s
T_e	Exhaust gas temperature measured during cone calorimeter tests	K
T_u	Unburned sample temperature at ignition measured by thermocouple	K

(continued on next page)

* Corresponding author.

E-mail address: ernesto.salzano@unibo.it (E. Salzano).

<https://doi.org/10.1016/j.jlp.2026.106156>

Received 22 April 2026; Received in revised form 17 July 2026; Accepted 11 August 2026

Available online 12 August 2026

0950-4230/© 2026 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

(continued)

T_F	Flame temperature measured by thermal imaging	K
V_r	Reactive volume involved in the oxidation process	m ³
x_{ox}	Oxygen molar fraction in exhaust gases during combustion	–
x_{ox}^0	Initial oxygen molar fraction in exhaust gases before combustion	–
YCO	Carbon monoxide yield	–
YCO ₂	Carbon dioxide yield	–
ρ	Density of the liquid sample	kg/m ³
sEHC	Steady-state effective heat of combustion	MJ/kg
sHRR	Steady-state heat release rate	kW/m ²
sMLR	Steady-state mass loss rate	g/s
sYCO	Steady-state carbon monoxide yield	–
sYCO ₂	Steady-state carbon dioxide yield	–

1. Introduction

Ethanolamines are largely used in gas sweetening (for CO₂ and H₂S), within the carbon capture, utilization, and storage technologies, in the cosmetic industry as emulsifiers and for pH controllers, as pretreatment agents, cement additives for grinding, corrosion inhibitors, and a reactant for the amidation reaction, in the production of surfactants and detergents (Dziejarski et al., 2023; Krzemień et al., 2016). The most relevant for industrial applications are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyl-diethanolamine (MDEA). These substances are easily oxidised and are thermally unstable, potentially undergoing oxidative or thermal degradation (de Ávila et al., 2015). Therefore, understanding the chain of events in degradation phenomena and the corresponding kinetics is paramount for proper handling of these substances and design of the industrial processes. For what concerns the degradation pathway, oxidative degradation produces carbon dioxide, water, ammonia, organic acids, and aldehydes following the reaction pathways described in the current literature (Khan et al., 2024; Léonard et al., 2014), whereas thermal degradation can lead to the formation of carbamate, urea, and heterocyclic compounds (Jorgensen et al., 2024a; Vevelstad et al., 2022). The formation of intermediates and the thermal stability of ethanolamines are strongly affected by the investigated conditions (de Ávila et al., 2015; Hatchell et al., 2014), as it can be observed for the case of the carbamate production, representing the initiation reaction of the thermal degradation, which occurs in one apparent step for the case of MEA and multiple steps for the case of DEA, forming ethylene oxide and MEA at first, as detailed in dedicated studies (Epp et al., 2011; Jorgensen et al., 2024b). Therefore, accurately understanding the behaviour of ethanolamines in reactive conditions is paramount to properly design industrial processes and safety measures (Van den Bogaert et al., 2025; Walters et al., 2016).

On the one hand, the kinetics of heterogeneous reactive systems can be evaluated through macroscopic parameters and overall apparent reactions. In this light, laboratory-scale analyses indicate that degradation of MEA, DEA, TEA, and MDEA in inert (nitrogen) and oxidative (air) environments presented a zero-order reaction (de Ávila et al., 2015; Léonard et al., 2014). The overall reaction rate and the corresponding kinetic parameters reported in the current literature (de Ávila et al., 2015) are listed in Table 1 for the sake of completeness.

Under these premises, the thermal stability has been assessed based on the activation energy of the overall reaction, as

Table 1

Kinetic parameters reported in the literature for the oxidative degradation of ethanolamines, namely the pre-exponential factor (k_0) and activation energy (E_a) derived from thermogravimetric measurements, as reported in the current literature (de Ávila et al., 2015).

Parameter	MEA	DEA	TEA	MDEA
k_0 [1/s]	$1.63 \cdot 10^5$	$9.36 \cdot 10^5$	$14.78 \cdot 10^5$	$1.09 \cdot 10^5$
E_a [kJ/mol]	47	63	68	49

TEA > DEA > MDEA > MEA (de Ávila et al., 2015). On the other hand, detailed kinetic mechanisms composed of a set of elemental reactions and intermediates can list the most relevant steps involving stable and radical species. Within this scope, different approaches can be employed for the development of kinetic mechanisms, including manual selection based on expert judgement and automatic selection based on dedicated algorithms (Pio et al., 2022). In gas-phase oxidation, ignition kinetics are typically governed by the rate-controlling initiation step that generates the first pool of radicals (Glassman and Yetter, 2008). At low temperatures, i.e., < 600 K, the dominant initiation pathway for several commonly investigated species is the hydrogen abstraction by small radicals, which produces radicals that subsequently undergo O₂ addition and chain-branching sequences, as detailed in dedicated studies (Battin-Leclerc, 2008; Curran, 2019). Under these conditions, abstracting agents that are relatively unimportant at high temperatures, such as OH, HO₂, or O₂, can become kinetically significant due to their higher concentration and favourable reaction energies, as indicated in the literature (Le et al., 2018; Zádor et al., 2011).

Regardless of the approach used to develop a kinetic model, the availability of a robust and comprehensive experimental dataset is essential for validation. In this sense, lab-scale thermogravimetric analysis has been largely employed for the assessment of the overall reaction rate (Venkatesh et al., 2013; Zhang, 2020). More recently, the use of bench-scale apparatuses has been promoted for the evaluation of heterogeneous systems, to better evaluate the effects of transport phenomena on the investigated reactions (De Liso et al., 2025a,b). In bench-scale thermogravimetric testing, the heat release rate (HRR) measured in a cone calorimeter is typically ruled by the initial decomposition process of the material, which controls the onset of volatile species generation, allowing the evaluation of the overall reactivity and exothermicity of different reactive systems (De Liso et al., 2024). This setup operates by exposing a material sample to a controlled radiant heat flux, obtained by using a conical electric heater, thereby inducing evaporation and/or pyrolysis under standardised conditions (Babrauskas, 1984, 2016). The current work presents the results of an experimental campaign devoted to the evaluation of the reactivity of MEA, DEA, TEA, and MDEA by means of a cone calorimeter. The collected data were employed for the identification of the rate-determining step and the quantification of a kinetic model suitable for the oxidative degradation of the investigated species. The resulting information can support the development of accurate models and, thus, allow for the identification of the optimal and safe operative conditions and for the optimisation of industrial processes involving amines.

2. Methodology

Pure ethanolamines, having a purity of >99%wt, were investigated in the present study. More specifically, MEA (Sigma Aldrich, 102877446), DEA (Sigma Aldrich, 102877960), TEA (Sigma Aldrich, 4104012844), and MDEA (Sigma Aldrich, 102809272) were tested.

To this aim, the cone calorimeter model *iCone plus* (Fire Testing Technology), designed in agreement with the indications included within the dedicated literature (Babrauskas, 2016; ISO 5660, 2019), was employed to characterise the oxidative behaviour of liquid samples placed in a 10 cm × 10 cm specimen located under a radiant heater. A schematic representation of the experimental setup, including the main components of the cone calorimeter configuration, is provided in Fig. 1.

An initial sample thickness of 1 cm was tested for all the investigated conditions. The tests were performed directly on the liquid-phase samples, which were initially placed in the specimen holder in the condensed state. Upon exposure to the external heat flux, evaporation of the liquid phase occurred, and the generated vapours subsequently sustained the gas-phase combustion process. A constant external heat flux was delivered from a conical-shaped resistance placed at 2.5 cm from the sample surface, while a continuous spark ignition of 10 kV was provided at 1 cm from the initial liquid surface. Different values of

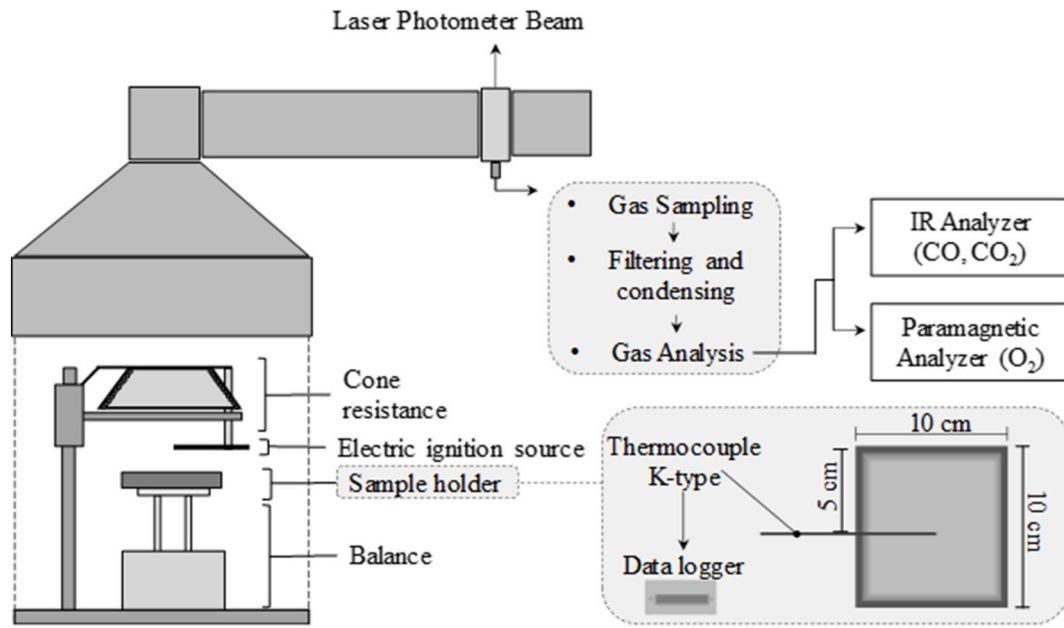


Fig. 1. Schematic representation of the cone calorimeter setup employed for the experimental analysis of liquid-phase samples.

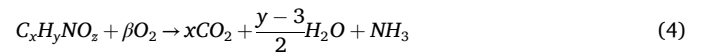
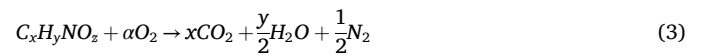
external heat flux between 12.5 and 50 kW/m² were tested. Although each condition was repeated three times, only the average values were reported for the sake of clarity since a limited variation (i.e., < 5%) was observed. Nevertheless, a summary of the whole set of experimental data is provided in the supplementary material. The sample mass and the Mass Loss Rate (MLR) were continuously measured by means of a load cell, whereas the optical sensors and gas sampling analysers for O₂ (paramagnetic analyser), CO (nondispersive infrared sensor), and CO₂ (nondispersive infrared sensor) were employed to continuously record parameters such as the Heat Release Rate (HRR, Equation (1)) (DiDomizio and Weckman, 2016), smoke production, and exhaust composition. Further details on the adopted system are available in the current literature (De Liso et al., 2024).

$$HRR = \frac{\Delta h_c}{r} \cdot \frac{M_{ox}}{M_{air}} \cdot C \cdot \sqrt{\frac{\Delta P}{T_e}} \cdot \frac{(x_{ox}^0 - x_{ox})}{(1 + (b-1)x_{ox}) - bx_{ox}} \quad (1)$$

where $\Delta h_c/r$ represents the heat released per mass of oxygen consumed, corresponding to 13.1 MJ/kg, M_{ox} and M_{air} are the molar weights of oxygen and air, C and b are calibration factor ($C \sim 0.04$ kg K^{0.5}/(atm^{0.5} s)) and instrument constant ($b \sim 1.1$) determined during blank tests performed in agreement with the dedicated standard (ISO 5660, 2019), T_e and ΔP are the exhaust conditions in terms of temperature and difference in pressure, and x_{ox}^0 and x_{ox} stand for the oxygen molar fractions before and during the tests of the exhaust streams. A dedicated protocol developed for calibration purposes was employed for the determination of the reported values of $\Delta h_c/r$, C , and b (Babrauskas, 2016; ISO 5660, 2019). These values were considered as constants for the whole experimental campaign. Conversely, the time-dependent values derived from the cone calorimeter were considered for the remaining parameters. In addition, the liquid temperature was monitored by means of a K-type thermocouple placed at the centre of the sample holder, whereas the gas-phase temperature profile was assessed by means of a Hikmicro thermal camera collocated at 0.60 m from the centre of the liquid-vapour interface. Additional information on the employed procedure can be found elsewhere (De Liso et al., 2025a,b). The measured liquid temperature was used to identify the thermal condition of the sample at ignition, which was considered representative for safety considerations. Based on the HRR and MLR collected once a stable flame is reached, the effective heat of combustion (EHC) was estimated (Equation (2)) for all the investigated conditions.

$$EHC = \frac{HRR}{MLR} \quad (2)$$

The resulting values were compared with the theoretical enthalpy of reaction (ΔH_r) calculated through dedicated databases (Burcat and Branko, 2005) under the assumption of complete conversion to CO₂, H₂O, and N₂ (Equation (3), $\Delta H_{r,N_2}$) and CO₂, H₂O, and NH₃ (Equation (4), $\Delta H_{r,NH_3}$), to identify the overall reaction and represent a conservative assumption for the evaluation of fire-related scenarios.



The overall reaction rate (r_a) was assessed based on the mass balance and the collected data (Equation (5)). More specifically, the laminar burning velocity (S_u) was calculated (Equation (6)) and employed for the assessment of the flame thickness (δ), following the one-dimensional chemical kinetic approach largely adopted in the current literature (Dahoe and de Goeij, 2003; Vancouillie et al., 2012). Then, the reactive volume (V_r) was estimated based on the unburned temperature (T_u), flame temperature (T_f), and temperature increase (dT/dt), as reported in Equation (7).

$$r_a = \frac{MLR}{M_{am} \cdot V_r} \quad (5)$$

$$S_u = \frac{MLR}{\rho \cdot A} \quad (6)$$

$$V_r = \delta \cdot A = \frac{T_f - T_u}{dT/dt} \cdot S_u \cdot A \quad (7)$$

where M_{am} , ρ , and A represent the molar weight of the investigated amine, the liquid density, and the surface of the sample holder.

The resulting r_a were compared with estimations deriving from empirical-based kinetic models available in the current literature (Léonard et al., 2014), indicated as $r_{a,Lit}$. In addition, theoretically-based reaction rates of H abstraction reactions were estimated considering the coefficients available in dedicated databases (Gao et al., 2016). Within this scope, as introduced in Section 1, OH, H, HO₂, and O₂ were

considered as the reference abstracting agents, and each possible abstracting site on the ethanolamine molecule was evaluated. Following the approach employed for the development of the aforementioned database, the modified Arrhenius equation, having the pre-exponential factor (k_0), the temperature exponent (n), and the activation energy (E_a) from the literature (Gao et al., 2016), was considered and an elemental kinetic was assumed, meaning that the order of reaction was assumed to be equal to one, either for the concentration of ethanolamine or the abstracting agent, reported respectively as [EtAm] and [AbAg]. For the sake of clarity, the definition of the theoretically based rate ($r_{a,Th}$) is reported in Equation (8).

$$r_{a,Th} = k_0 \cdot T_u^n \cdot e^{\left(-\frac{E_a}{R \cdot T_u}\right)} \cdot [\text{EtAm}] \cdot [\text{AbAg}] \quad (8)$$

Notably, T_u was used in the Arrhenius term as the kinetic analysis was performed under ignition conditions, considering the thermal state of the unburned mixture at the onset of the combustion process. This approach allows the reaction rate to be evaluated based on the conditions experienced by the reacting species prior to flame development, rather than on the temperature reached after combustion. The initial content of amine in the gas phase was assumed equal to the lower flammability limit (LFL) reported within the safety data sheets, whereas the initial content of oxygen was considered 21%v. The T_F and T_u were identified as the maximum temperature in the gas phase observed by the thermal camera and the temperature measured by the thermocouple at the ignition time, respectively.

3. Results and discussion

The measured HRR and MLR of pure amines exposed to an external heat flux of 12.5, 25.0, and 50.0 kW/m² are shown in Figs. 2–4.

As evident from Figs. 2–4, similar trends are observed for the investigated species when exposed to different external heat fluxes. Indeed, the HRR and MLR profiles exhibit a single dominant combustion stage, indicating a relatively simple burning behaviour primarily governed by rapid volatilisation and gas-phase oxidation rather than multi-step condensed-phase degradation. The absence of secondary HRR peaks suggests a limited formation of thermally stable intermediates or char residues, which is consistent with the low aromaticity and weak cross-linking propensity of aliphatic amines. A nearly constant EHC is

observed throughout the burning period, with values consistent with the corresponding theoretical heats of combustion, indicating high combustion efficiency and negligible incomplete oxidation phenomena. Furthermore, the temporal coincidence between the onset of MLR and HRR rises suggests that fuel vaporisation and gas-phase combustion are tightly coupled, with minimal thermal lag or transport limitations within the condensed phase. This behaviour implies that the burning process is primarily controlled by surface vaporisation driven by external heat feedback, rather than by diffusion-limited degradation kinetics within the liquid bulk.

Additional temperature measurements revealed higher temperatures when the thermocouple was positioned closer to the liquid–gas interface, indicating the presence of thermal stratification within the liquid layer. This stratification is likely promoted by the relatively high viscosity of certain amines, which suppresses natural convection and leads to non-uniform temperature fields across the sample depth. Consequently, the upper liquid layer experiences enhanced heating due to both conductive heat transfer from the bulk and thermal feedback from the flame. In particular, radiative and convective heat transfer from the flame locally increases the net heat flux at the liquid surface, potentially causing surface superheating and promoting accelerated vaporisation. From an engineering perspective, the observed steady MLR plateau before flame extinction reflects a quasi-steady burning regime in which the imposed external heat flux, internal thermal stratification, and flame-to-surface heat feedback jointly control the regression rate and the overall burning dynamics. The high solubility and relatively low tendency to form thermally stable residues further contribute to homogeneous degradation and smooth HRR and MLR profiles, with no evidence of oscillatory or multi-stage burning behaviour. A significant increase in HRR and MLR can be observed when ethanolamines are exposed to increasing heat fluxes in the experimental runs (see Table 2). Conversely, this parameter shows a negligible effect on the EHC, meaning that the increase in the external heat flux does not affect the gas-phase chemistry but only the evaporation rate, resulting in positive feedback on the rate of heat production. This behaviour is confirmed by the analysis of combustion products since CO yields remained within a narrow range for all investigated conditions (0.002–0.007), despite the increase in burning intensity at higher heat fluxes, with no systematic increase as a function of the imposed thermal load. This confirms that the enhanced combustion rate is mainly associated with increased fuel vaporisation rather than with a shift towards incomplete oxidation

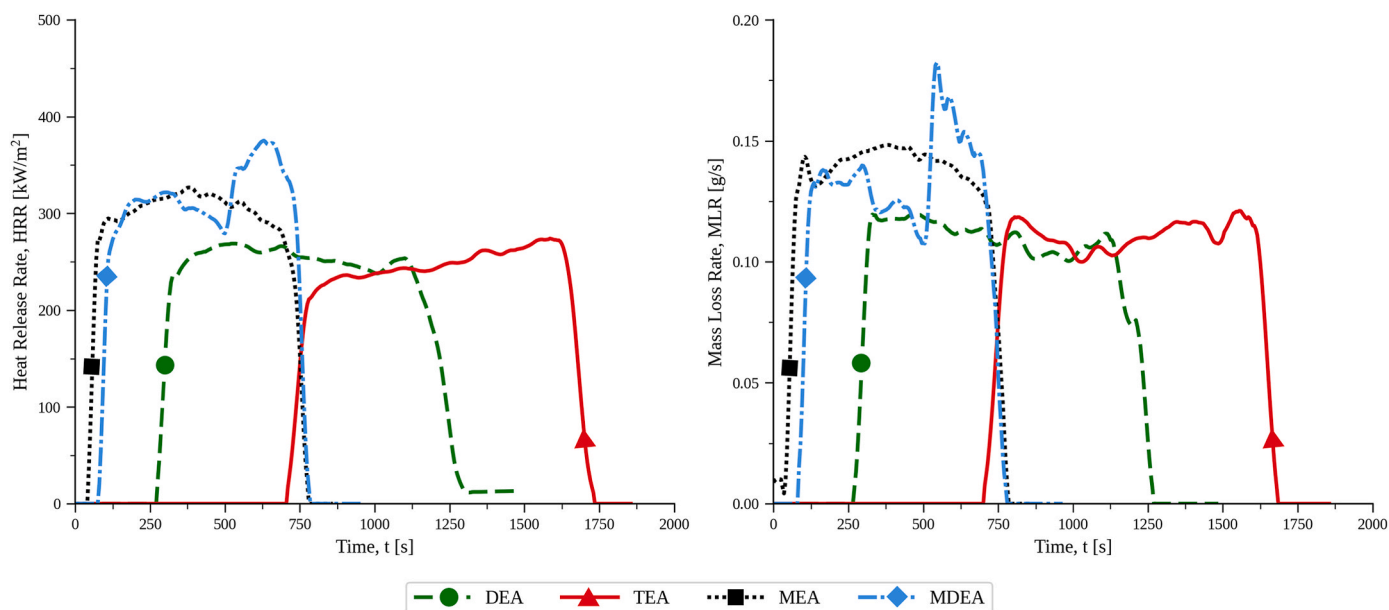


Fig. 2. Measured time evolution of heat release rate (left) and mass loss rate (right) of pure amine exposed to an external heat flux of 12.5 kW/m².

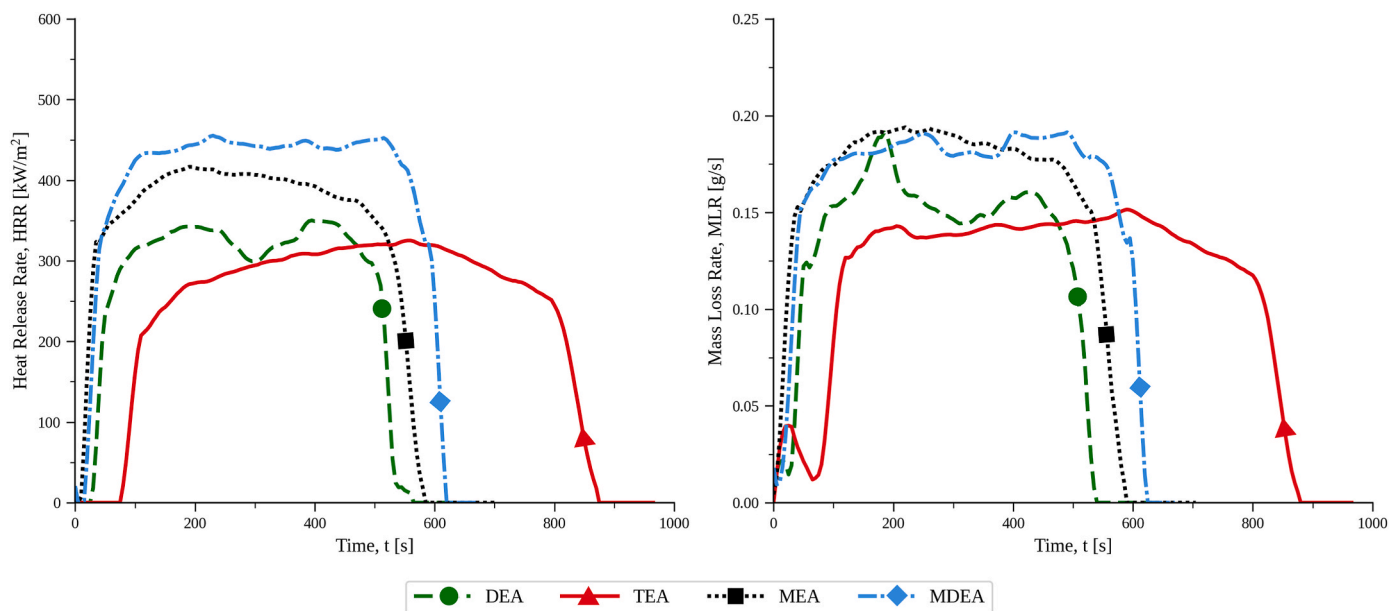


Fig. 3. Measured time evolution of heat release rate (left) and mass loss rate (right) of pure amine exposed to an external heat flux of 25.0 kW/m².

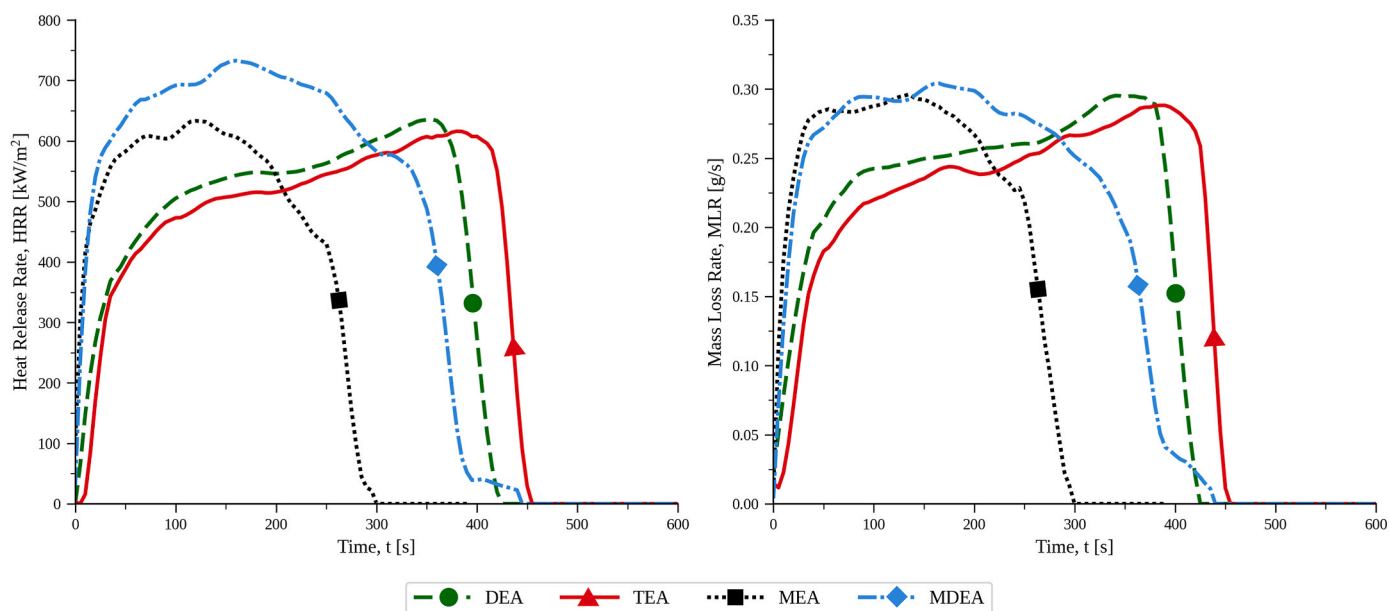


Fig. 4. Measured time evolution of heat release rate (left) and mass loss rate (right) of pure amine exposed to an external heat flux of 50.0 kW/m².

pathways.

The obtained values of sEHC are falling within the range defined by $\Delta H_{r,N_2}$ and $\Delta H_{r,NH_3}$. It is worth noting that CO formation was detected during the experimental tests ($Y_{CO} > 0$); however, the corresponding CO yields were approximately three orders of magnitude lower than the CO₂ yields under all investigated conditions. Therefore, $\Delta H_{r,N_2}$ and $\Delta H_{r,NH_3}$, which represent the heat produced by the complete oxidation of carbonaceous species to CO₂, were considered representative of the apparent kinetic rate.

The overall reaction rates derived from the cone calorimeter ($r_{a,Cone}$) were estimated and compared in Table 3 with data from lab-scale testing available in the current literature (de Ávila et al., 2015) ($r_{a,Lit}$). The theoretical reaction rates ($r_{a,Th}$) obtained by the procedure described in the methodology section are also reported, allowing for the identification of the most relevant initiation reaction kinetics and showing a good

estimation quality of the experimental data collected in this work, especially for the cases of TEA and MDEA.

Regardless of the abstracting site, reactions considering O₂ as the abstracting agent were found to have a significantly lower kinetic rate than that recorded in the experiments (<6 orders of magnitude). This confirms that direct molecular oxygen abstraction is kinetically negligible under the investigated fire-relevant conditions, where radical-mediated pathways are expected to dominate the early oxidation stages (Turns Stephen R., 2011). Therefore, specific considerations on the kinetics of H abstraction by small radicals are reported below. Indeed, the ruling abstracting agents and sites are affected by the amine structure. Similarly, the kinetics of different abstracting sites are discussed in view of the investigated conditions. In this sense, it is worth noting that, although the intrinsic bond dissociation energies (BDEs) of N–H and α -C–H bonds in aliphatic amines are similar, literature evidence indicates that α -C–H bonds are generally slightly weaker and that

Table 2

Steady-state values of Heat Release Rate (sHRR), Mass Loss Rate (sMLR), Effective of combustion (sEHC), and Carbon monoxide and Carbon dioxide Yields (sYCO, sYCO₂), directly obtained by cone calorimeter at different heat fluxes, and the heat of reaction considering the production of N₂ ($\Delta H_{r,N_2}$) and the NH₃ ($\Delta H_{r,NH_3}$).

12.5 kW/m ²	MEA	DEA	TEA	MDEA
sHRR [kW/m ²]	320.7	262.5	276.4	314.3
sMLR [g/s]	0.147	0.113	0.114	0.124
sEHC [MJ/kg]	21.75	23.10	24.29	25.30
$\Delta H_{r,N_2}$ [MJ/kg]	21.80	24.30	25.30	26.10
$\Delta H_{r,NH_3}$ [MJ/kg]	17.80	22.00	23.70	24.10
sYCO [-]	0.004	0.004	0.007	0.005
sYCO ₂ [-]	1.206	1.433	1.549	1.552
25 kW/m ²	MEA	DEA	TEA	MDEA
sHRR [kW/m ²]	411.6	345.0	345.5	449.0
sMLR [g/s]	0.192	0.155	0.143	0.184
sEHC [MJ/kg]	21.48	22.25	24.16	24.40
$\Delta H_{r,N_2}$ [MJ/kg]	21.80	24.30	25.30	26.10
$\Delta H_{r,NH_3}$ [MJ/kg]	17.80	22.00	23.70	24.10
sYCO [-]	0.003	0.003	0.004	0.006
sYCO ₂ [-]	1.219	1.195	1.460	1.577
50 kW/m ²	MEA	DEA	TEA	MDEA
sHRR [kW/m ²]	619.6	627.2	631.8	715.0
sMLR [g/s]	0.291	0.283	0.276	0.289
sEHC [MJ/kg]	21.32	22.15	22.86	24.76
$\Delta H_{r,N_2}$ [MJ/kg]	21.80	24.30	25.30	26.10
$\Delta H_{r,NH_3}$ [MJ/kg]	17.80	22.00	23.70	24.10
sYCO [-]	0.002	0.004	0.004	0.004
sYCO ₂ [-]	1.231	1.450	1.523	1.558

Table 3

Reaction rates experimentally obtained in this work ($r_{a,Cone}$), deriving from experimental data available in the current literature ($r_{a,Lit}$), and from theoretical estimations ($r_{a,Th}$) at the ignition temperature.

	MEA	DEA	TEA	MDEA
$r_{a,Cone}$ [kmol/m ³ /s]	0.68	0.26	0.15	0.39
$r_{a,Lit}$ [kmol/m ³ /s]	0.41	0.48	0.09	0.76
$r_{a,Th}$ [kmol/m ³ /s]	0.33	0.47	0.12	0.45

abstraction at this position leads to the formation of α -amino carbon-centred radicals stabilised by lone-pair assisted interactions (captodative effect) and inductive contribution (Lalevée et al., 2002). However, under oxidative conditions, the effective pathway was found to be governed not solely by bond strength but also by the kinetic selectivity of the abstracting radical and transition-state effects. More specifically, for the cases of MEA and DEA, the experimental kinetics are well represented by the H abstraction from the nitrogen sites by HO₂. This observation is consistent with recent computational studies on primary amines, which show that the barrier and rate of H abstraction are highly dependent on the radical and on the site of abstraction (Liu et al., 2025). The dominance of this pathway can be rationalised considering the relatively selective nature of HO₂ radicals and the polar character of the N–H bond, potentially lowering the activation barrier in low-to-intermediate temperature oxidation regimes. Actually, the H abstractions from the carbon site by HO₂ and H are representative of the TEA and MDEA kinetics, respectively. In these tertiary amines, the absence of N–H bonds and the increased alkyl substitution enhance stabilisation of the resulting α -amino carbon-centred radicals through inductive and hyperconjugative effects, thereby favouring carbon-site abstraction under combustion conditions (Shang and Luo, 2024).

The gathered information represents an essential step for the development and validation of detailed kinetic mechanisms suitable for the characterisation of the oxidative degradation of ethanolamines. Indeed, the relevance of H abstraction and the identification of ruling abstracting agents for the determination of the ignition behaviour under the investigated conditions guide and promote dedicated investigations

to obtain accurate estimations of their kinetics through advanced numerical approaches, such as *ab initio* calculations using high levels of theory, essential for a proper selection of the most relevant reaction pathways and intermediates. It is worth noting that the present investigation was performed at bench scale under controlled external heat flux conditions, and the obtained parameters should be interpreted considering the inherent limitations of cone calorimeter measurements. In particular, the extrapolation of these results to large-scale scenarios, such as pool fires, storage tanks, or accidental releases in industrial environments, requires specific considerations due to the influence of scale-dependent phenomena, including fuel spreading, ventilation conditions, and flame feedback.

4. Conclusions

This study presents the results of a comprehensive experimental campaign using a cone calorimeter to investigate the oxidative degradation of selected ethanolamines under varying external heat fluxes. The resulting dataset enabled the determination of the most relevant parameters for the evaluation of the flame behaviour of the investigated substances. The results demonstrated that increasing external heat flux primarily enhanced the burning intensity by accelerating fuel volatilisation, while the combustion efficiency remained nearly unchanged, as indicated by the limited variation of EHC values. Besides, based on the collected data, apparent kinetic rates were developed together with indications on possible deviations in the case of incomplete oxidation. The comparison among the investigated ethanolamines highlighted that hazard assessment should consider both the energy release during combustion and the intrinsic reactivity at ignition conditions. In particular, the measured reaction rates revealed different oxidation propensities among the compounds, whereas the cone calorimeter measurements identified the conditions leading to the highest thermal release. The resulting model was subsequently validated against empirical observations derived from the literature and theoretically based predictions of rates. The limited contribution of incomplete oxidation pathways, confirmed by the substantially lower CO yields compared with CO₂ formation, indicates that the main fire-related concern for these compounds is associated with heat release rather than CO production under the investigated conditions. This integrated analysis allowed the identification of the rate-determining steps governing the oxidative pathways of pure ethanolamines. Such insights are essential for ensuring the safe handling of hazardous species as well as the realisation of accurate reactive models for supporting the robust design of industrial processes in which these compounds are stored, processed, or thermally stressed. Eventually, the gathered information can also be used as the basis for the development of accurate models and correlations assessing the effects of initial composition on the kinetic and safety aspects of ethanolamines, extending the applicability of these findings to additional industrial applications.

CRedit authorship contribution statement

Benedetta A. De Liso: Data curation, Formal analysis, Investigation, Writing – original draft. **Matteo Curcio:** Visualization, Writing – review & editing. **Gianmaria Pio:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Valerio Cozzani:** Funding acquisition, Resources, Supervision, Writing – review & editing. **Ernesto Salzano:** Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jlp.2026.106156>.

Data availability

Data will be made available on request.

References

- Babrauskas, V., 1984. Development of the cone calorimeter? A bench-scale heat release rate apparatus based on oxygen consumption. *Fire Mater.* 8, 81–95. <https://doi.org/10.1002/fam.810080206>.
- Babrauskas, V., 2016. The Cone Calorimeter. *SFPE Handbook of Fire Protection Engineering*, Fifth Edition, pp. 952–980. https://doi.org/10.1007/978-1-4939-2565-0_28.
- Battin-Leclerc, F., 2008. Detailed chemical kinetic models for the low-temperature combustion of hydrocarbons with application to gasoline and diesel fuel surrogates. *Prog. Energy Combust. Sci.* 34, 440–498. <https://doi.org/10.1016/j.pecs.2007.10.002>.
- Burcat, A., Branko, R., 2005. Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with Updates from Active Thermochemical Tables. <https://doi.org/10.2172/925269>, Technical Report ANL-05/20, ANL-05/20 TAE 960.
- Curran, H.J., 2019. Developing detailed chemical kinetic mechanisms for fuel combustion. *Proc. Combust. Inst.* 37, 57–81. <https://doi.org/10.1016/j.proci.2018.06.054>.
- Dahoe, A.E., de Goey, L.P.H., 2003. On the determination of the laminar burning velocity from closed vessel gas explosions. *J. Loss Prev. Process. Ind.* 16, 457–478. [https://doi.org/10.1016/S0950-4230\(03\)00073-1](https://doi.org/10.1016/S0950-4230(03)00073-1).
- de Ávila, S.G., Logli, M.A., Matos, J.R., 2015. Kinetic study of the thermal decomposition of monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) and methyl-diethanolamine (MDEA). *Int. J. Greenh. Gas Control* 42, 666–671. <https://doi.org/10.1016/j.ijggc.2015.10.001>.
- De Liso, B.A., Pio, G., Chanut, C., Salzano, E., 2025a. Determining the kinetic of the oxidation of metallic solid particles. *Chem. Eng. J.* 514, 163164. <https://doi.org/10.1016/j.cej.2025.163164>.
- De Liso, B.A., Pio, G., Salzano, E., 2024. Fire behaviour of liquid solvents for energy storage applications. *Process Saf. Environ. Prot.* 188, 726–734. <https://doi.org/10.1016/j.psep.2024.05.153>.
- De Liso, B.A., Pio, G., Salzano, E., 2025b. Experimental and advanced numerical characterization of toluene fires. *Fuel* 397, 135448. <https://doi.org/10.1016/j.fuel.2025.135448>.
- DiDomizio, M.J., Weckman, E.J., 2016. An evaluation of methodologies for determining delay times in the cone calorimeter fire test. *J. Test. Eval.* <https://doi.org/10.1520/JTE20140401>.
- Dziejarski, B., Krzyżyńska, R., Andersson, K., 2023. Current status of carbon capture, utilization, and storage technologies in the global economy: a survey of technical assessment. *Fuel* 342, 127776. <https://doi.org/10.1016/j.fuel.2023.127776>.
- Epp, B., Fahlenkamp, H., Vogt, M., 2011. Degradation of solutions of monoethanolamine, diglycolamine and potassium glycinate in view of tail-end CO₂ absorption. *Energy Proc.* 4, 75–80. <https://doi.org/10.1016/j.egypro.2011.01.025>.
- Gao, C.W., Allen, J.W., Green, W.H., West, R.H., 2016. Reaction mechanism generator: automatic construction of chemical kinetic mechanisms. *Comput. Phys. Commun.* 203, 212–225. <https://doi.org/10.1016/j.cpc.2016.02.013>.
- Glassman, I., Yetter, R.A., 2008. *Combustion*, fourth ed. Elsevier, San Diego, California.
- Hatchell, D., Namjoshi, O., Fischer, K., Rochelle, G.T., 2014. Thermal degradation of linear amines for CO₂ capture. *Energy Proc.* 63, 1558–1568. <https://doi.org/10.1016/j.egypro.2014.11.165>.
- ISO 5660, 2019. ISO 5660-1: 2019. Reaction-to-fire Tests. Heat Release, Smoke Production and Mass Loss Rate Heat Release Rate (Cone Calorimeter Method) and Smoke Production Rate (Dynamic Measurement).
- Jorgensen, T.B., Liu, K., Thompson, J.G., 2024a. Examining the reactions of ethanolamine's thermal degradation compounds in carbon capture through ¹H NMR and ¹³C NMR. *Ind. Eng. Chem. Res.* 63, 10863–10878. <https://doi.org/10.1021/acs.iecr.3c04019>.
- Jorgensen, T.B., Liu, K., Thompson, J.G., 2024b. Examining the reactions of Ethanolamine's thermal degradation compounds in carbon capture through ¹H NMR and ¹³C NMR. *Ind. Eng. Chem. Res.* 63, 10863–10878. <https://doi.org/10.1021/acs.iecr.3c04019>.
- Khan, A., Yasin, S., Mahmood, H., Afzal, S., Iqbal, T., 2024. Advanced oxidative degradation of monoethanolamine in water using ultraviolet light and hydrogen peroxide. *RSC Adv.* 14, 33223–33232. <https://doi.org/10.1039/D4RA05590J>.
- Krzemiński, A., Wieckol-Ryk, A., Smoliński, A., Koterka, A., Wieclaw-Solny, L., 2016. Assessing the risk of corrosion in amine-based CO₂ capture process. *J. Loss Prev. Process. Ind.* 43, 189–197. <https://doi.org/10.1016/j.jlp.2016.05.020>.
- Lalevée, J., Allonas, X., Fouassier, J.P., 2002. N-H and α(C-H) bond dissociation enthalpies of aliphatic amines. *J. Am. Chem. Soc.* 124, 9613–9621. <https://doi.org/10.1021/ja0204168>.
- Le, X.T., Mai, T.V.T., Lin, K.C., Huynh, L.K., 2018. Low temperature oxidation kinetics of biodiesel molecules: rate rules for concerted HO₂ elimination from Alkyl Ester peroxy radicals. *J. Phys. Chem. A* 122, 8259–8273. <https://doi.org/10.1021/acs.jpca.8b05070>.
- Léonard, G., Töye, D., Heyen, G., 2014. Experimental study and kinetic model of monoethanolamine oxidative and thermal degradation for post-combustion CO₂ capture. *Int. J. Greenh. Gas Control* 30, 171–178. <https://doi.org/10.1016/j.ijggc.2014.09.014>.
- Liu, M., Chen, M., Fan, R., Liao, Y., Wang, J., Zhou, C.W., Tian, Z.Y., 2025. Combustion kinetics of amines: exploring hydrogen atom abstraction reactions from primary amines by NH₂ radicals. *Proc. Combust. Inst.* 41. <https://doi.org/10.1016/j.proci.2025.105832>.
- Pio, G., Dong, X., Salzano, E., Green, W.H., 2022. Automatically generated model for light alkene combustion. *Combust. Flame* 241, 112080. <https://doi.org/10.1016/j.combustflame.2022.112080>.
- Shang, Y., Luo, S.N., 2024. Insights into the role of the H-abstraction reaction kinetics of amines in understanding their degeneration fates under atmospheric and combustion conditions. *Phys. Chem. Chem. Phys.* 26, 20167–20215. <https://doi.org/10.1039/d4cp02187h>.
- Turns, Stephen R., 2011. *An Introduction to Combustion Concepts and Applications*.
- Van den Bogaert, A., Verplaetsen, F., Vanierschot, M., Braeken, L., Leblebici, M.E., 2025. Carbon capture with pure monoethanolamine aerosols: method development for assessing safety hazards and identifying a safe operating window using oxygen-containing flue gas streams. *J. Loss Prev. Process. Ind.* 94. <https://doi.org/10.1016/j.jlp.2025.105587>.
- Vancoillie, J., Demuynck, J., Galle, J., Verhelst, S., van Oijen, J.A., 2012. A laminar burning velocity and flame thickness correlation for ethanol–air mixtures valid at spark-ignition engine conditions. *Fuel* 102, 460–469. <https://doi.org/10.1016/j.fuel.2012.05.022>.
- Venkatesh, M., Ravi, P., Tewari, S.P., 2013. Isoconversional kinetic analysis of decomposition of nitroimidazoles: friedman method vs flynn–wall–ozawa method. *J. Phys. Chem. A* 117, 10162–10169. <https://doi.org/10.1021/jp407526r>.
- Vevelstad, S.J., Buvik, V., Knuutila, H.K., Grimstvedt, A., Da Silva, E.F., 2022. Important aspects regarding the chemical stability of aqueous amine solvents for CO₂ capture. *Ind. Eng. Chem. Res.* 61, 15737–15753. <https://doi.org/10.1021/acs.iecr.2c02344>.
- Walters, M.S., Edgar, T.F., Rochelle, G.T., 2016. Regulatory control of amine scrubbing for CO₂ capture from power plants. *Ind. Eng. Chem. Res.* 55, 4646–4657. <https://doi.org/10.1021/acs.iecr.6b00318>.
- Zádor, J., Klippenstein, S.J., Miller, J.A., 2011. Pressure-dependent OH yields in alkene + HO₂ reactions: a theoretical study. *J. Phys. Chem. A* 115, 10218–10225. <https://doi.org/10.1021/jp2059276>.
- Zhang, X., 2020. Applications of kinetic methods in thermal analysis: a review. *Eng. Sci.* <https://doi.org/10.30919/es8d1132>.