

Membrane Reactors for Plastic and Biomass Waste Valorisation: A Critical Review

M. Jafari¹, A. Andarz¹, G. Bagnato², K. Ghasemzadeh^{3*}

¹ School of Chemical Engineering, College of Engineering, University of Tehran, Tehran 1417614418, Iran

² KORE Group, School of Engineering, Lancaster University, Lancaster, LA1 4BY, UK

³ School of Engineering, University of Edinburgh, Edinburgh EH8 9YL, UK

* Correspondence: kghasemz@ed.ac.uk

1. Introduction

The overlay visualization shown in Figure S1 depicts the chronological development of research related to membrane reactors for biomass and plastic waste valorization from 2000 to 2025. The color gradient—from blue to yellow—illustrates the shift from early fundamental studies to more recent, application-focused advancements. Earlier research (blue–green areas) mainly focused on biomass conversion, anaerobic digestion, and wastewater treatment, with initial attention on the biological and environmental aspects of membrane bioreactors. Conversely, the yellow-colored nodes, representing recent years, cluster around terms such as membrane reactor, steam reforming, hydrogen production, and biofuels, indicating a distinct research movement toward catalytic and thermo-chemical valorization methods. This timeline reveals an increasing focus on process intensification, hydrogen production, and integrated reaction–separation systems with advanced membranes. Overall, the overlay map emphasizes the dynamic growth of this field—from foundational environmental biotechnology to innovative hybrid reactor designs aimed at efficient waste-to-fuel conversion and circular carbon utilization.

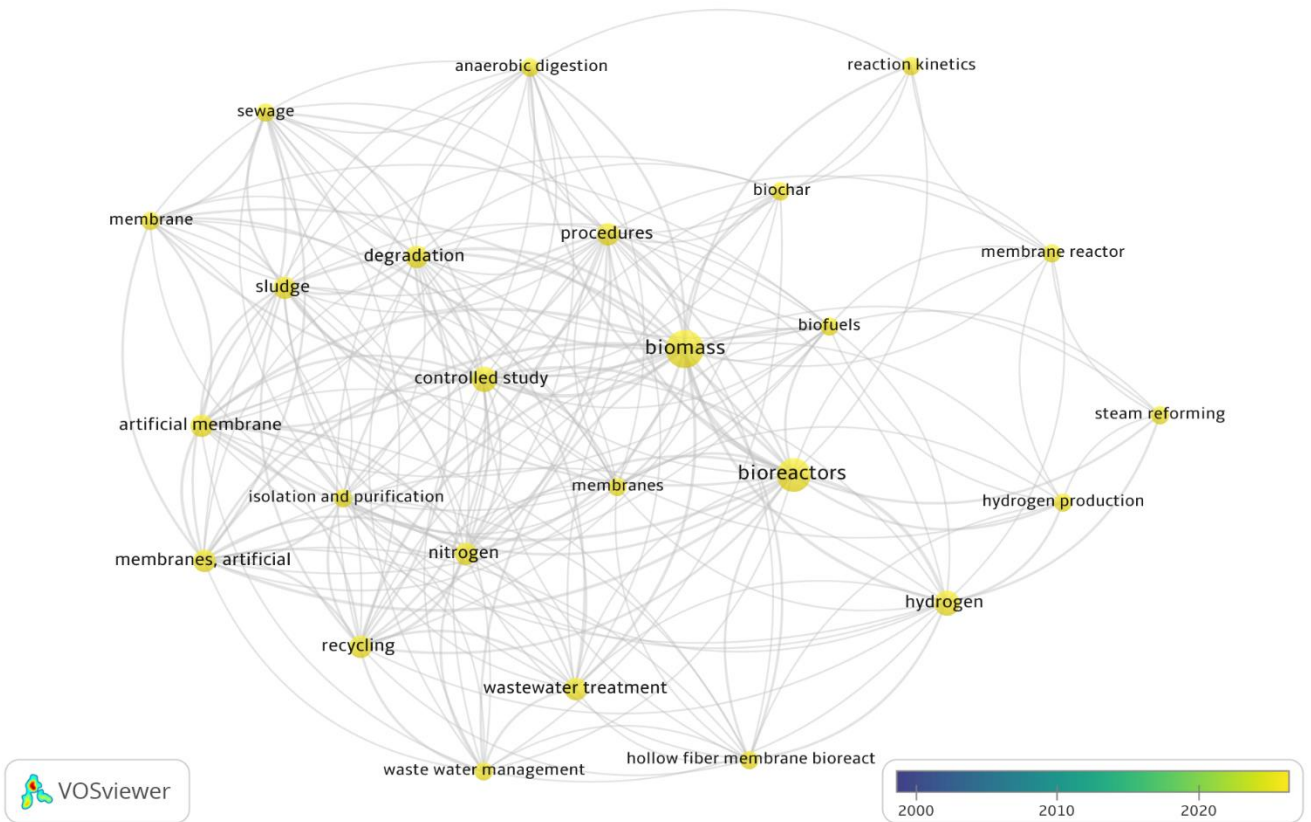


Figure S1. Overlay visualization of keyword co-occurrence in studies on membrane reactors for biomass and plastic waste valorization, illustrating the temporal development of research themes from 2000 to 2025.

Unlike the Network Visualization, which shows the conceptual relationships among keywords, and the Overlay Visualization, which displays the chronological development of research themes, the Density Visualization in Figure S2 emphasizes the intensity and focus of research activity within the field. The yellow areas mark the highest keyword density, indicating the most commonly studied topics. In this map, the main hotspots are biomass and bioreactors, highlighting that core research focuses on biological processes and the use of membrane reactors in biomass conversion and biofuel production. On the other hand, the green-to-blue zones indicate emerging or less-explored topics, such as hydrogen production, membrane reactors, and steam reforming, and demonstrate increasing research interest in catalytic membrane systems for the thermochemical valorization of plastic and biomass waste.

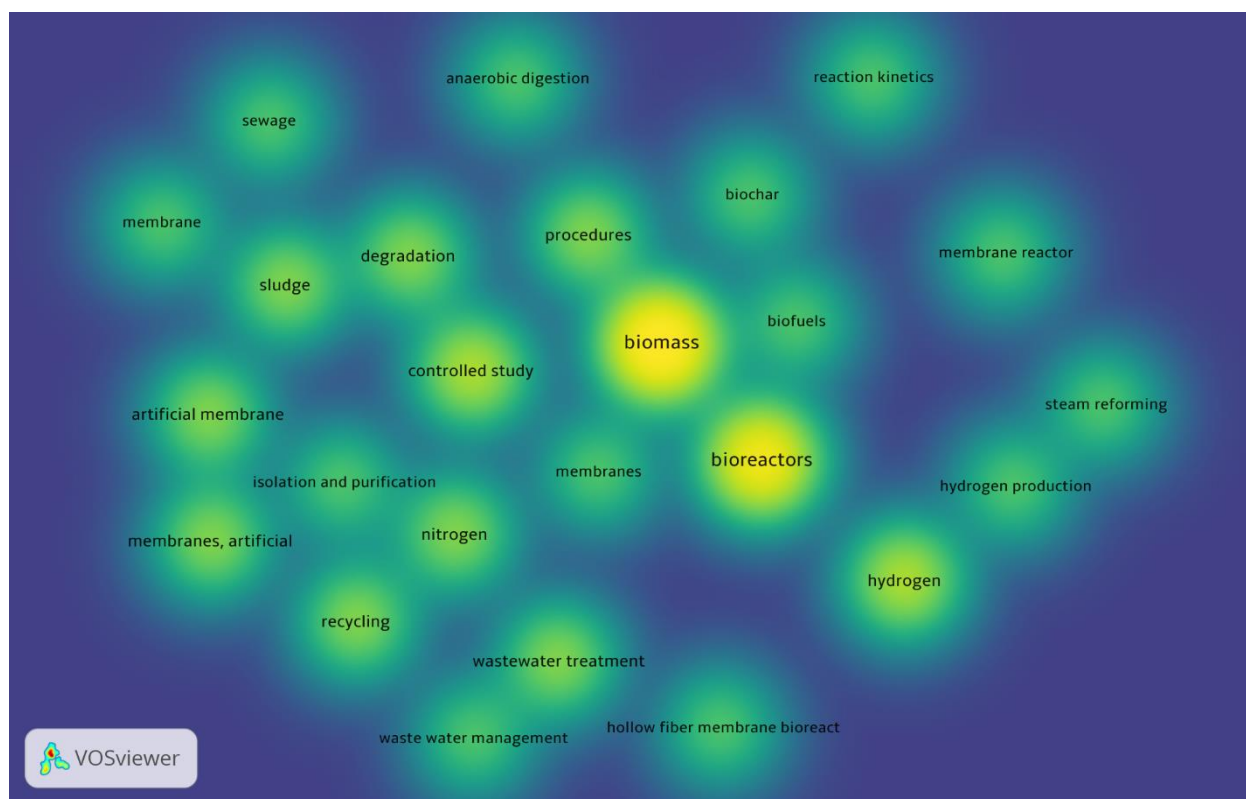


Figure S2. Density visualization of keyword co-occurrence in studies on membrane reactors for biomass and plastic waste valorization, highlighting the concentration and intensity of research activity across thematic areas.

3. Catalysts in Membrane Reactor Systems

Table S1 provides a comprehensive overview of membrane materials and transport characteristics that have been investigated for plastic and biomass valorisation across a wide range of operating environments. The table highlights the strong predominance of dense metallic and ceramic membranes for high-temperature hydrogen separation, particularly Pd-based and Pd–Ag systems, which operate under reforming-relevant conditions and rely on solution–diffusion-controlled hydrogen transport. In contrast, polymeric and composite membranes are predominantly applied in low-temperature or liquid-phase processes, including pervaporation, ultrafiltration, and membrane bioreactor configurations, where separation of water, liquid intermediates, or depolymerisation products governs process performance. The diversity of membrane classes summarized in Table S1 illustrates how membrane material selection, thickness, and operating window are closely tailored to the physicochemical nature of plastic- and biomass-derived streams, ranging from gas-phase hydrogen-rich mixtures to aqueous and multiphase reaction environments.

Table S1. Membrane materials and transport characteristics used in plastic and biomass valorisation.

Membrane material	Membrane class	Transported species	Thickness (μm)	Operating T / P	Ref.
Pd-based	Dense metallic	H ₂	2–20	350–500 °C; ≤30 bar	[1]
Silica (SiO ₂)	Microporous ceramic	H ₂	–	240–573 K; ΔP 0.5–1.5 bar	[1]
Pd–Ag	Dense metallic	H ₂	<3–20	375–500 °C; ΔP ≤470 kPa	[1]
Ceramic (TiO ₂ /Al ₂ O ₃)	Porous ceramic	Water (pervaporation)	—	60–70 °C; ~1 bar	[1]
Polyimide	Dense polymeric	Water	—	135 °C; ~1 bar	[1]
Polyacrylonitrile (PAN)	Polymeric (MBR)	Reaction products	—	<60 °C; ~1 bar	[1]
PET, PS, PVC, PE, PP	Dense polymeric	Gas separation	–	–	[2]
Nafion™ 117	Dense polymer electrolyte	H ⁺	183	50–80 °C; electrolysis cell	[3]
Stainless steel	Dynamic membrane support	Microplastics retention	100–300	Ambient; gravity-driven	[4]
PS UF	Dense polymeric (UF)	Liquid species	150	Ambient; 1 bar	[5]
HDPE	Dense polymeric (sintered)	Liquid species	–	Filtration 0.85 bar; sintering 180 °C	[6]
Keratin/PEO NF	Polymeric nanofibrous	Liquid species	–	RT	[7]
Cellulose/PVDF UF	Polymeric composite	Liquid species	–	RT	[7]
CNC	Biopolymeric UF	Liquid species	–	RT	[7]
Regenerated cellulose UF	Polymeric UF	PEG	150	RT	[7]
CA NF	Polymeric NF	Oil/water	–	RT	[7]
PVC UF	Polymeric UF	Humic acid	–	RT	[7]
PET NF	Polymeric NF	Water vapour	–	100–160 °C (post-treat)	[7]

Rubber NF composite	Composite NF	Dyes	–	RT	[7]
Carbon molecular sieve (CMS)	Dense carbon membrane	H ₂	–	250–350 °C; 3–5 bar	[8]
UF (PET MBR)	Ultrafiltration membrane	PET hydrolysis products	–	–	[9]
UF cellulose	Ultrafiltration membrane	TPA, MHET, protons	–	–	[9]

Table S2 summarizes the diverse reaction–separation mechanisms that govern the performance of membrane-based systems applied to plastic and biomass valorisation under markedly different physicochemical environments. Across thermochemical membrane reactors, in-situ hydrogen removal emerges as a dominant intensification strategy, enabling equilibrium shifting and enhanced conversion beyond conventional reactor limits in reforming and water–gas shift processes, albeit often constrained by intrinsic reaction kinetics or transport resistances. In contrast, low-temperature and liquid-phase membrane systems rely primarily on size exclusion, adsorption, or diffusive product removal mechanisms to retain macromolecular species, microplastics, or inhibitory reaction products, where performance is frequently limited by fouling, cake-layer formation, or membrane stability. The comparison presented in Table S2 highlights how the effectiveness of membrane integration is strongly mechanism-dependent, with the membrane not only acting as a separator but also fundamentally reshaping reaction pathways, conversion limits, and process bottlenecks across both plastic- and biomass-derived feedstocks.

Table S2. Reaction/separation mechanisms in membrane systems.

Feedstock	System	Dominant mechanism	Effect of membrane	Limiting feature	Ref.
Biomass-derived biochar	Pyrolysis + MR	In-situ H ₂ removal	↑ H ₂ recovery	Pyrolysis kinetics	[1]
CH ₄ / alcohols	Reforming MR	Equilibrium shift	Conversion > equilibrium	Heat/mass transfer	[1]
PMMA model molecule	PEM electrolysis	Electro-oxidative C–O bond cleavage	Proton transport → H ₂	Catalyst poisoning	[3]
Microplastics	GD-DMF	Dynamic cake formation	MP retention	DM stability	[4]
Humic acid	UF	Cake filtration	Flux decline	Cake resistance	[5]
HDPE membrane	MF	Size exclusion + fouling layer	↑ rejection	Pore blocking	[6]
Wool keratin NF	Filtration	Adsorption + size exclusion	High dye removal	Fouling	[7]
PET NF (MD)	Membrane distillation	Vapour transport	High salt rejection	Wetting	[7]

Biomass-derived syngas	WGS membrane reactor	In-situ H ₂ removal (equilibrium shift)	CO conversion beyond the packed-bed reactor	Sweep gas ratio / ΔP	[8]
PET	Membrane bioreactor	Inhibitory-product removal	Enhanced enzymatic hydrolysis	Membrane biofouling	[9]
PET	Dialysis reactor	Diffusive in situ product removal	Increased depolymerisation and TPA yield	Membrane fouling / stability	[9]

Table S3 compiles representative operating conditions and performance metrics reported for membrane-based systems applied to plastic and biomass waste processing across gas- and liquid-phase environments. The studies summarized in the table demonstrate that membrane performance is highly process-specific, with gas-phase applications at elevated temperatures primarily targeting hydrogen recovery or equilibrium enhancement, while low-pressure liquid-phase systems focus on high fluxes, rejection efficiencies, or improved conversion yields in separation- or bioreactor-based configurations. Despite the wide variation in feedstocks and operating windows, the data in Table S3 collectively indicate that membrane-assisted systems can deliver substantial performance gains—such as enhanced hydrogen recovery, high contaminant rejection, or accelerated depolymerisation—when membrane materials and operating conditions are appropriately matched to the physicochemical characteristics of plastic- and biomass-derived streams.

Table S3. Operating conditions and performance of membrane systems.

Feedstock	Process	Membrane material	T / P	Performance metric	Ref.
Waste PET	Filtration	PET membrane	≤ 100 °C	50–350 LMH bar ⁻¹	[2]
Waste PS	Gas separation	PS membrane	1–5 bar	37–67 Barrer CO ₂	[2]
Waste PVC	UF	PVC membrane	–	BSA rej. up to 99 %	[2]
Waste PP	Oil–water sep.	PP membrane	–	Oil flux 10 000–15 000 LMH	[2]
PMMA	Electrolysis	Nafion™ PEM	50–80 °C	E _a 42.6–55.9 kJ.mol ⁻¹	[3]
PRF wastewater MPs	GD-DMF	SS + DM	Ambient	MP removal 97–99 %	[4]
Waste PS	UF	PS UF membrane	1 bar	Flux 166.6 LMH; HA rej. 84 %	[5]
River water	MF	HDPE membrane	0.85 bar	Size-dependent rejection	[6]
Waste PET bottles	MD	PET NF	100–160 °C	Salt rej. >99.9 %	[7]
Biomass-derived syngas	WGS-MR	CMS membrane	~300 °C; 3–5 bar	CO conversion >95%; H ₂ recovery >70%	[8]
PET	Enzymatic hydrolysis (MBR)	UF membrane	–	~70% higher hydrolysis efficiency vs batch	[9]
PET	Dialysis-assisted depolymerisation	UF cellulose membrane	–	>2× PET conversion and TPA yield	[9]

Table S4 highlights the strong interdependence between membrane structure, dominant transport properties, and overall process performance across a wide range of plastic and biomass valorisation applications. The comparison shows that key membrane attributes—such as hydrogen selectivity in dense metallic and carbon-based membranes, molecular sieving in silica systems, or hydrophilicity and porosity control in polymeric and nanofibrous membranes—directly determine achievable conversion, separation efficiency, and process stability. At the same time, the table illustrates that performance is often constrained by structure-specific limitations, including sealing degradation in Pd-based membranes, fouling and wetting phenomena in polymeric and nanofiltration systems, or reduced permeability at suboptimal operating temperatures. As summarized in Table S4, these structure–performance relationships are highly sensitive to feedstock characteristics, with hydrocarbon-rich reforming streams, oxygenated biomass-derived syngas, and plastic depolymerisation media imposing distinct constraints on membrane durability and functionality. This emphasizes that effective membrane reactor design requires careful alignment of membrane material properties with the physicochemical nature of the targeted plastic or biomass feedstock.

Table S4. Structure–performance relationships of membranes.

Membrane material	Key property	Limiting phenomenon	Performance impact	Sensitive feedstock	Ref.
Pd-based membranes	High H ₂ selectivity	Sealing/degradation	Equilibrium shift	Reforming feeds	[1]
Silica membranes	Molecular sieving	Mass transfer	H ₂ purity	Reforming feeds	[1]
PET-based membranes	Solvent resistance	Processability	Stable filtration	Waste PET	[2]
Nafion™ PEM	High proton conductivity	Catalyst poisoning at high voltage	Enables low-voltage H ₂ production	PMMA-derived organics	[3]
Dynamic membrane	Self-forming cake	Layer detachment	High MP retention	PRF MPs	[4]
PS UF membrane	Tunable porosity	Cake fouling	High HA rejection	Wastewater	[5]
HDPE membrane	Particle-controlled porosity	Fouling	↑ rejection	River water	[6]
Keratin NF	Hydrophilicity	Mechanical stability	High dye removal	Wool waste	[7]
PET NF (MD)	Thermal stability	Wetting	High salt rejection	Saline water	[7]
Rubber NF composite	Hydration layer	Layer densification	Antifouling	Dye wastewater	[7]
CMS membrane	H ₂ -selective dense structure	Reduced permeability at low T	Enables single-step WGS + separation	Biomass syngas	[8]
UF membrane (MBR)	Enables removal of inhibitory products	Biofouling/cleaning demand	Improved enzymatic PET hydrolysis	PET	[9]
UF cellulose membrane (dialysis)	Enzyme retention + product diffusion	Fouling and long-term stability	Higher depolymerisation and TPA yield	PET	[9]

4. Techno-Economic and Environmental Assessment

Table S5 provides a comprehensive overview of the key reactions that can be carried out in ion-conducting ceramic membrane reactors, including partial oxidation, oxidative coupling, steam and dry reforming, and water and carbon dioxide splitting. In addition to the reaction equations, the table reports the standard reaction enthalpies and typical operating temperature ranges, highlighting the strongly endothermic or exothermic nature of these processes and their high-temperature requirements. As shown in Table S1, such membrane reactors offer a versatile platform for the production of hydrogen, syngas, and value-added hydrocarbons under intensified process conditions.

Table S5. Reactions that can be performed in ion-conducting ceramic membrane reactors [10].

Reaction	Reaction Equation	ΔH^0 (kJ.mol ⁻¹)	Temperature (°C)
Partial oxidation of methane	$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	-36	850 – 900
Oxidative coupling of methane	$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$	-177	688 – 955
	$2CH_4 + \frac{1}{2}O_2 \rightarrow C_2H_6 + H_2O$	-282	
Oxidative dehydrogenation of hydrocarbons	$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$	-105	700 – 850
	$C_3H_8 + \frac{1}{2}O_2 \rightarrow C_3H_6 + H_2O$		
Water splitting reaction	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$	-242	900
Alkane to olefin reaction	$2CH_4 \rightarrow C_2H_6 + H_2$	71.1	750 – 900
	$2CH_4 \rightarrow C_2H_4 + 2H_2$	57.2	
Carbon dioxide decomposition	$2CO_2 \rightarrow 2CO + O_2$	552	> 900
Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	210	800
	$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$	256	
Dry reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	260.5	700 – 1000
	$6CH_4 \rightarrow C_6H_6 + 3H_2$	531	
Dehydroaromation of methane	$6CH_4 + \frac{9}{2}O_2 \rightarrow C_6H_6 + 9H_2O$	-1846	700 – 750

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