Reevaluating Green Solvent Metrics Using End-of-Life Considerations

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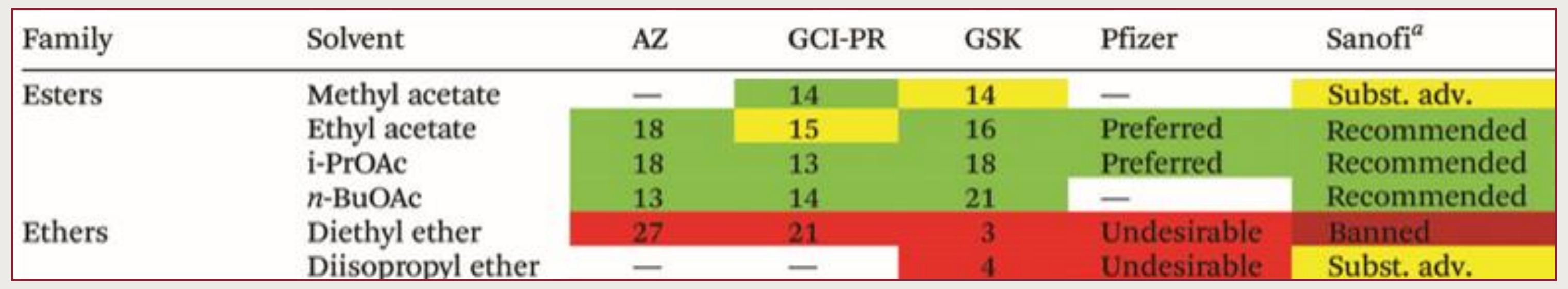
Abstract

Up to 90% of the mass used in industrial processes are solvents, while **only ~50% of solvents are recycled**.[1] Virgin solvent production is energetically demanding, and often has adverse environmental effects. Efficiently disposing of or recycling solvent waste from chemical processes is crucial to minimize industrial energy use. The goal of this research is to determine a simple but robust metric utilizing **thermophysical properties** to better evaluate the end-of-life considerations for solvents, creating more sustainable chemical processes.

Background & Motivation

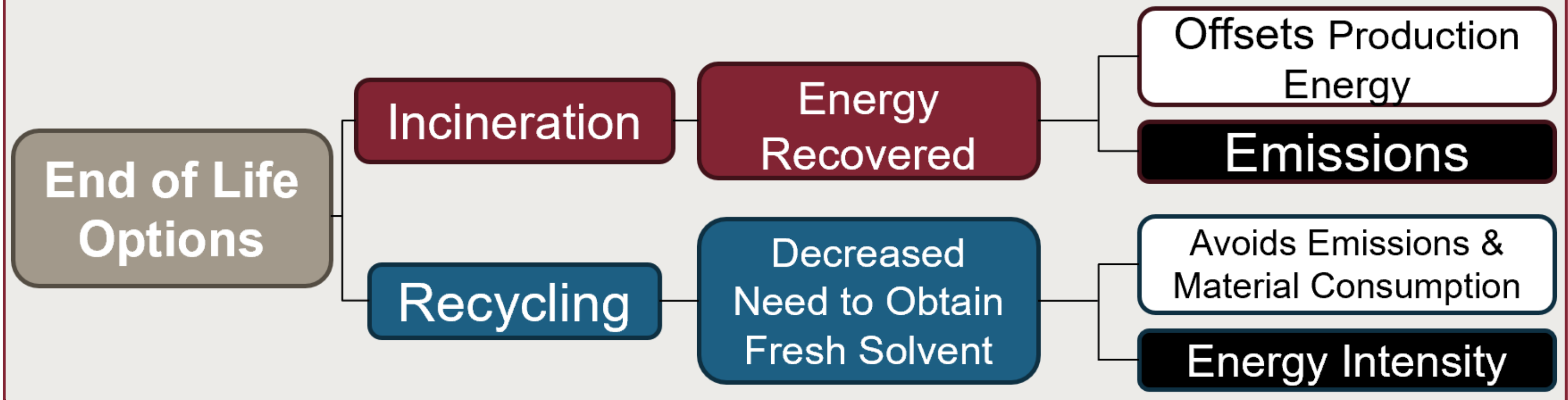
GREEN SOLVENTS: Ranked by environmental, health, and safety factors due to physicochemical properties via **solvent selection guides**.[2]



Family	Solvent	AZ	GCI-PR	GSK	Pfizer	Sanofi[a]
Esters	Methyl acetate	—	14	14	—	Subst. adv.
	Ethyl acetate	18	15	16	Preferred	Recommended
	i-PrOAc	18	13	18	Preferred	Recommended
	n-BuOAc	13	14	21	—	Recommended
Ethers	Diethyl ether	27	21	3	Undesirable	Banned
	Diisopropyl ether	—	—	4	Undesirable	Subst. adv.

Fig. 1. Discrepancies in solvent selection guide EHS rankings

END OF LIFE: Processing required to **recycle** or **dispose** of solvent after use. and associated emissions.



End of Life Options

Incineration

Energy Recovered

Offsets Production Energy

Emissions

Recycling

Decreased Need to Obtain Fresh Solvent

Avoids Emissions & Material Consumption

Energy Intensity

Fig. 2: End-of-life processing options, pros(white), cons(black)

Only widely-used **recyclability metric**:

- Boiling temperature (implying distillation heat-duty).

Full process design analyses for solvent recycling:

- Extensive, iterative, and requires large databases.

PROCESS IMPACTS: How solvent use affects the efficiency and end-of-life requirements of a process.

- Process impacts must be **balanced** with solvent greenness to minimize the process's **cumulative energy demand** (**CED**; energy used/saved/recovered).

OBJECTIVE: Calculate minimum separation energies (Q_{min}) using distillation and OSRO for equimolar, binary solvent mixtures with IPA and water as reference solvents.

Recycling: Distillation

Distillation exhibits higher energy demands as component boiling temperatures approach each other.

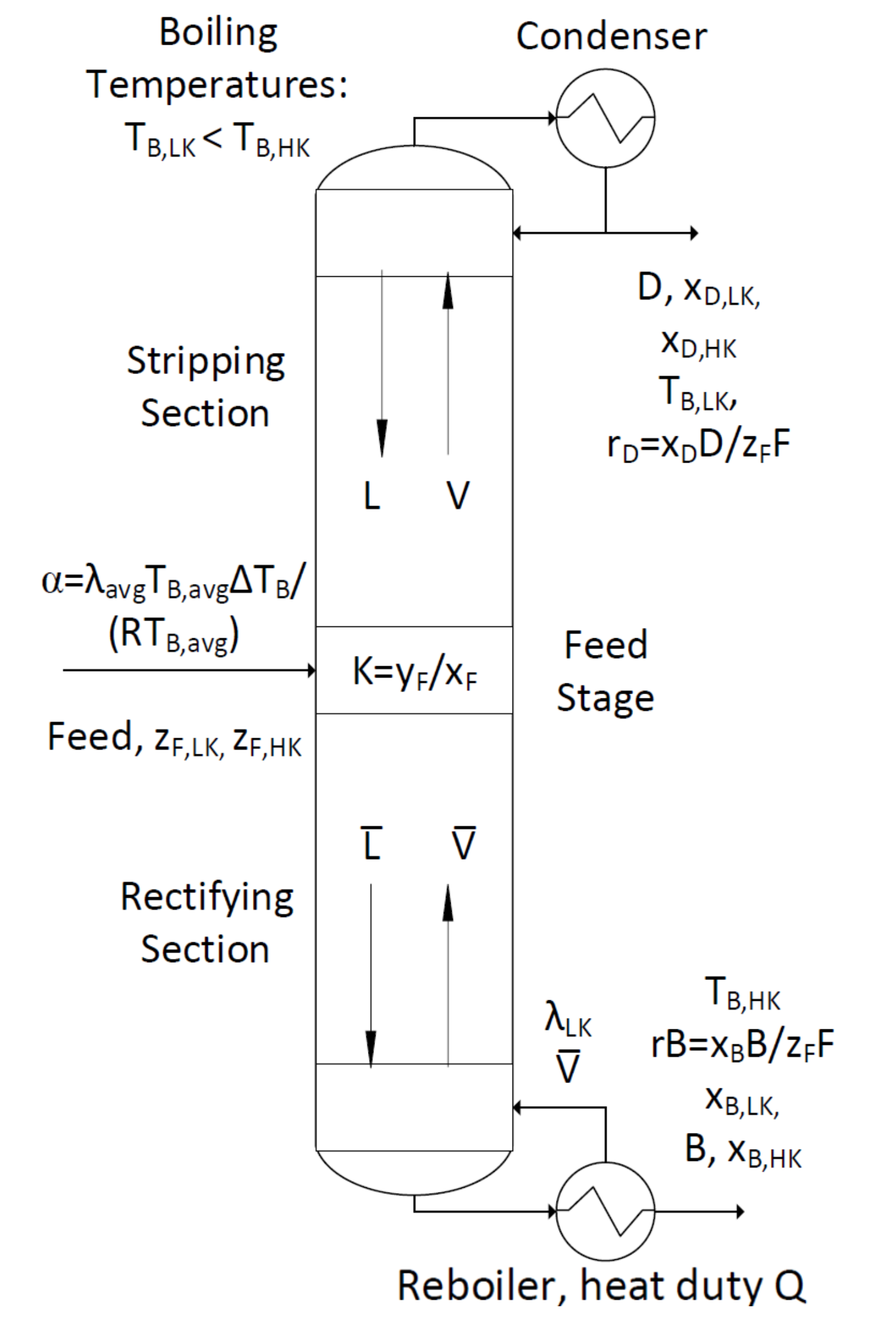


Fig. 3. Distillation Column, Eqs

$$Q_{min} = \lambda_{LK} \bar{V}_{min} = \lambda_{LK} \left(F \left(\frac{r_{D,i} - \alpha_{i,j} r_{D,i}}{\alpha_{i,j} - 1} \right) + D \right)$$

Eq. 1: King's Equation (relative volatility α, heat of vaporization λ, and distillate solvent recovery $r_{D,i}$) calculates Q_{min} at the **minimum column reflux**.[3]

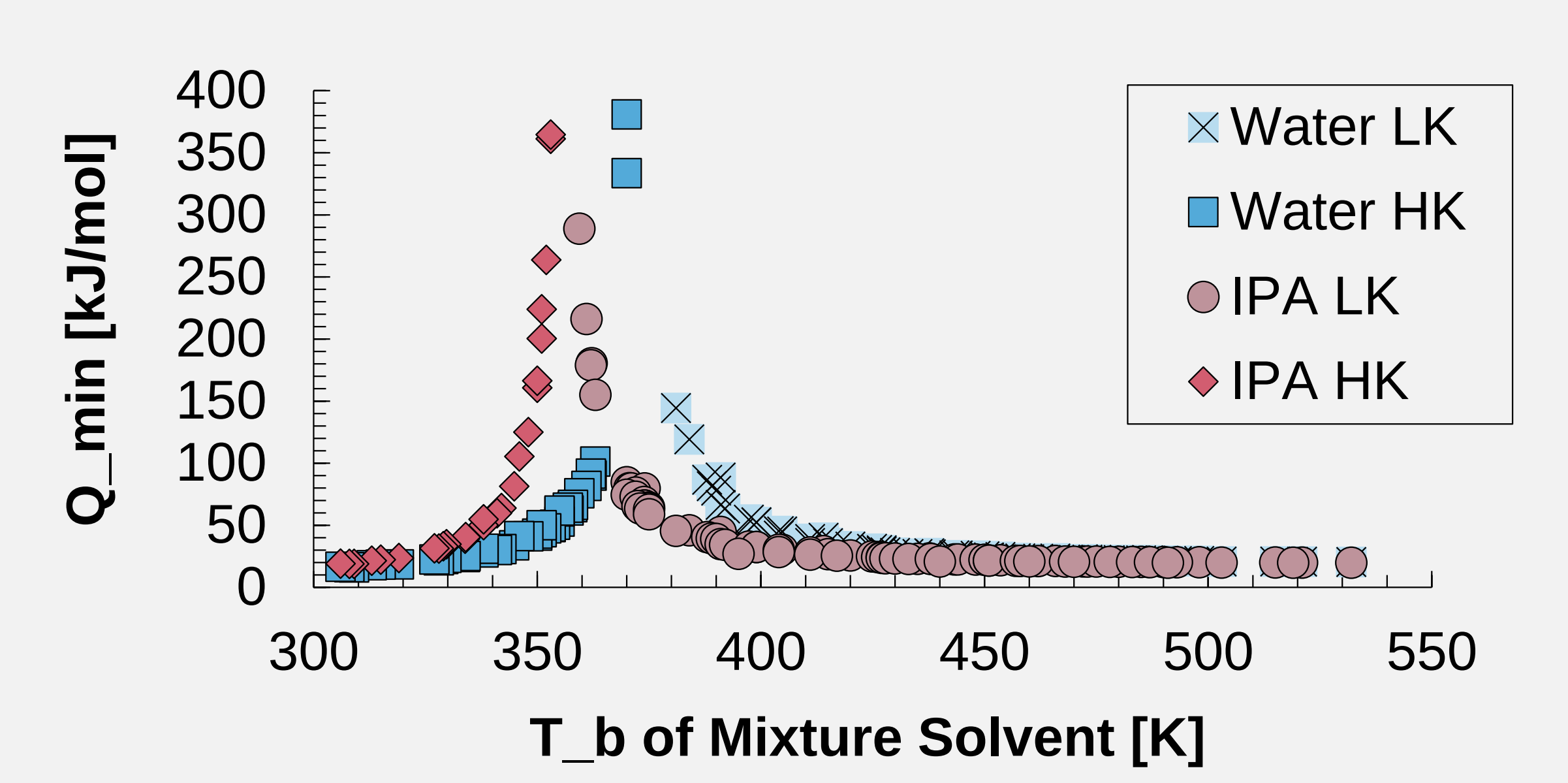


Fig. 4. Q_{min} depends strongly on **δBoiling Point** (T_b) between the mixture components.

Recycling: Organic Solvent Reverse Osmosis

OSRO energy demand is not dictated by molecular weight, but by permeability P_M: polarity δ_p, viscosity η, and solvent diameter d_m.

Eq. 2: Solvent $\{P_M\}$ via membrane constant "K"[4] is used to solve J_i[5] via **solution diffusion** mechanism.

$$J_i = \left\{ K \frac{\delta_p}{\eta d_m^2} \right\} \left[x_{i,F} - x_{i,p} \exp\left(\frac{\frac{MW_i}{\rho_i} \Delta P}{-RT} \right) \right]$$

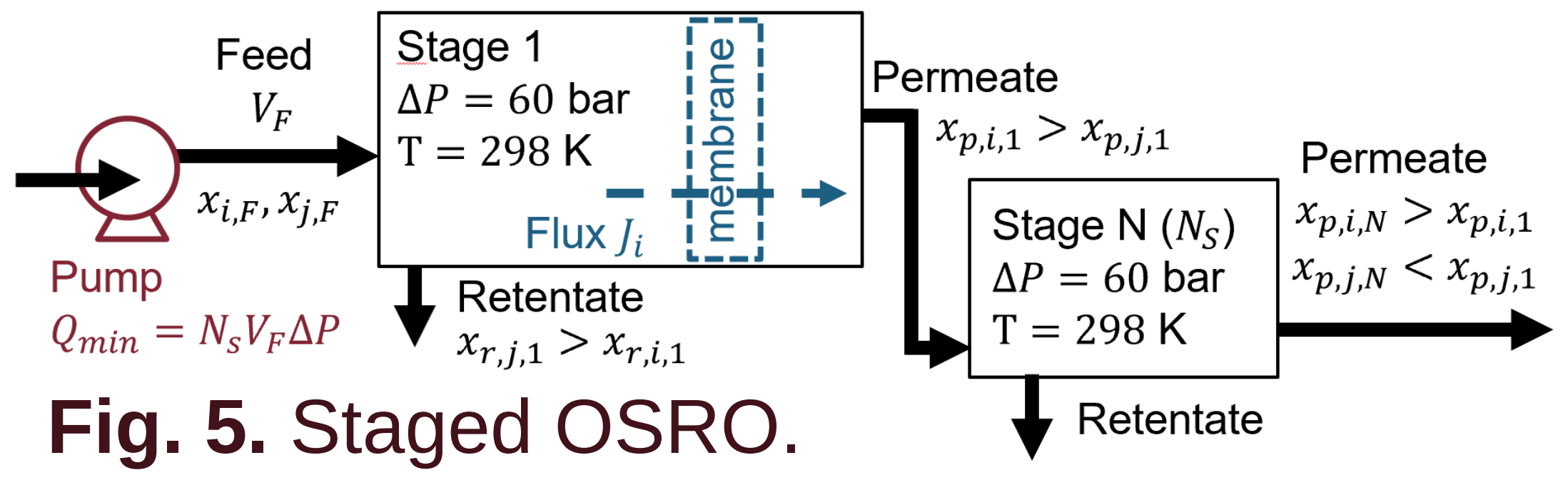
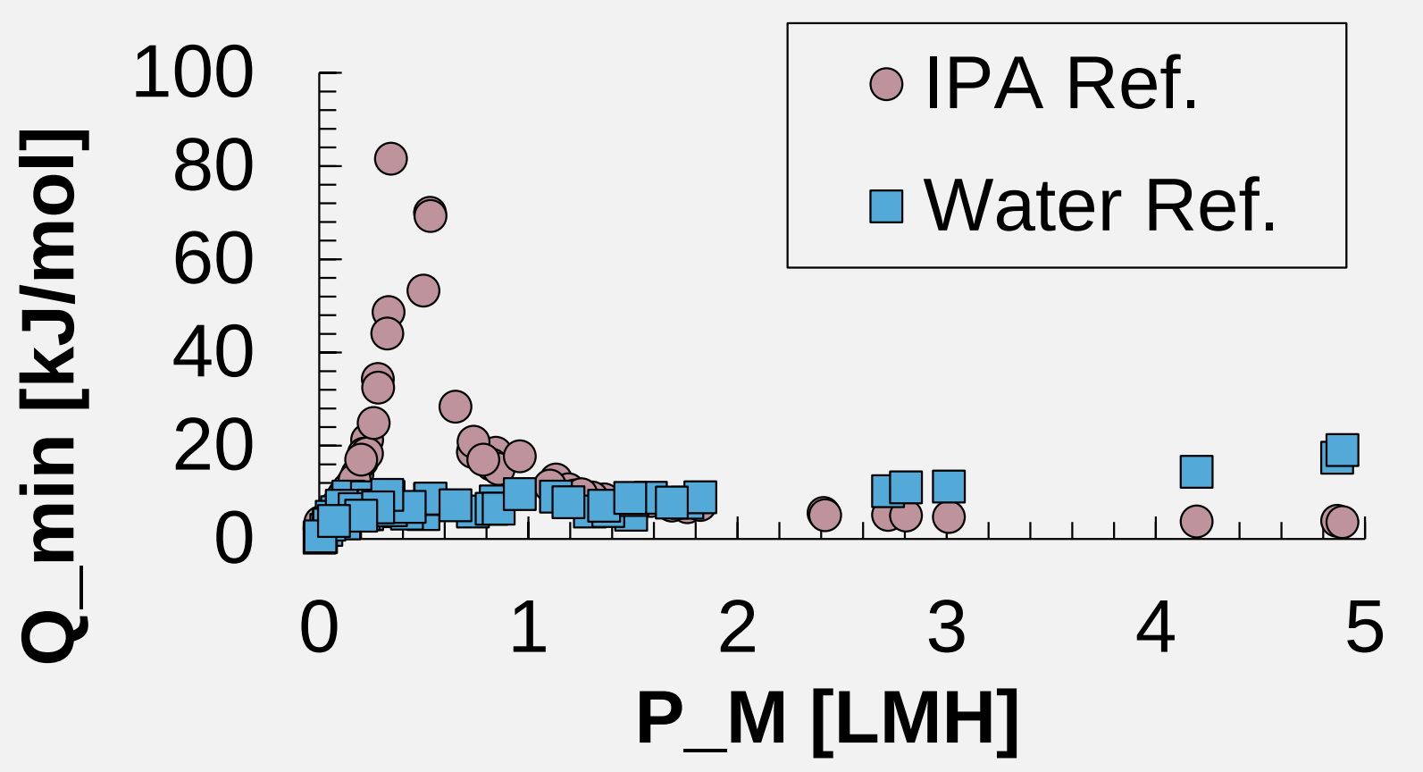
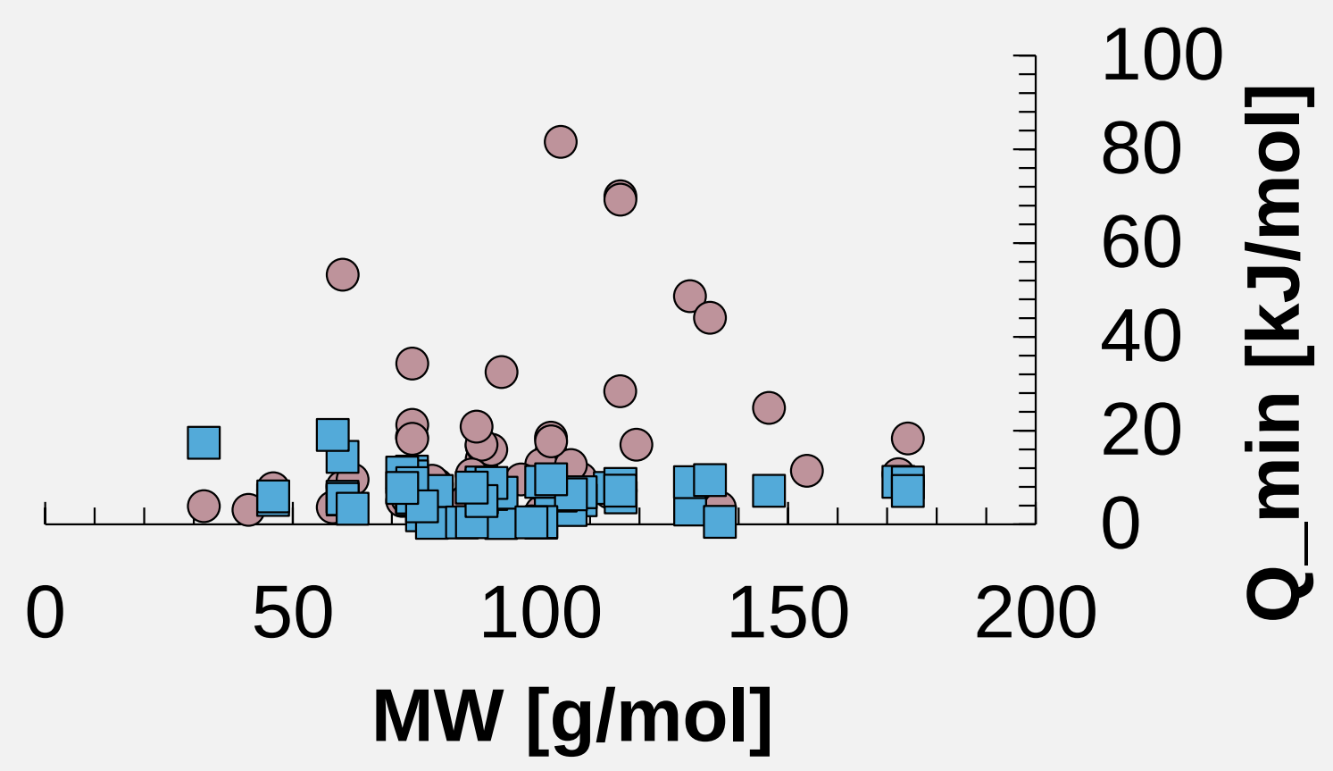


Fig. 5. Staged OSRO.



(L) Fig. 6: Q_{min} depends on δP_M.

(R) Fig. 7: Q_{min} lacks a clear trend with MW.



Disposal: Incineration

Energy return via incineration offsets energy demand of production.[6]

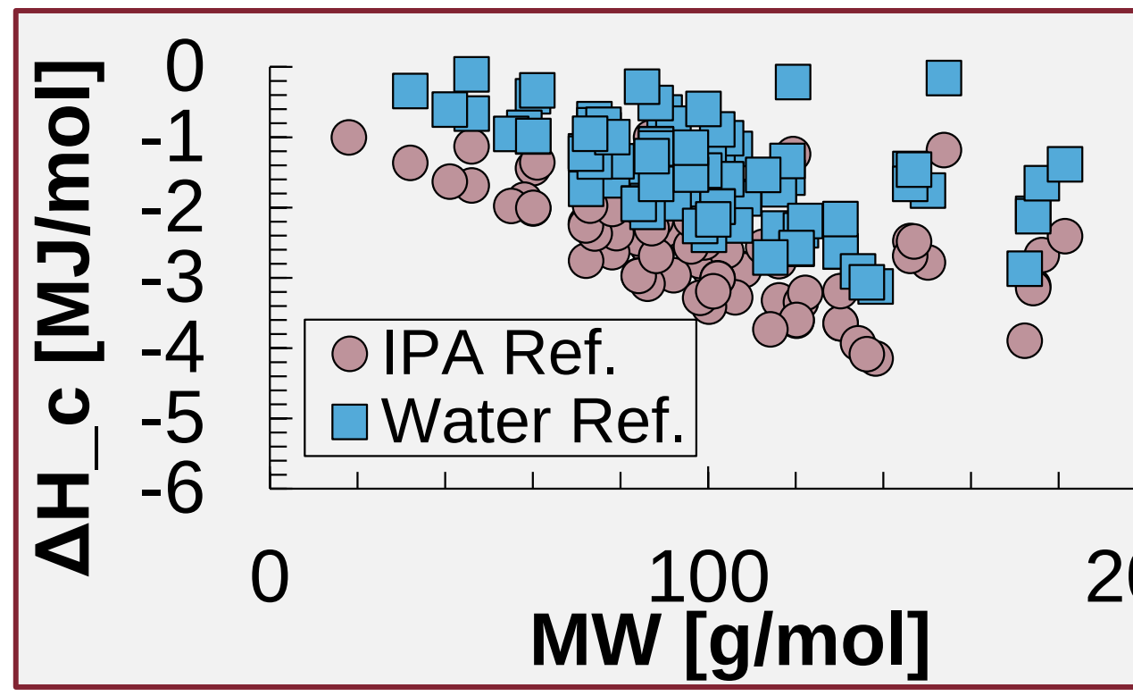


Fig. 8: Greater energy return for **larger** molecules

Table 1. CED_{incin} for single solv. recovery

Recovered Solvent	Methanol	IPA
$Q_{Incineration}$ [kJ/mol]	-726	-2005
$Q_{Production}$ [kJ/mol][7]	1304	3943
Sum: $CED_{incin.}$ [kJ/mol]	578	3910

Cumulative Energy Demand

Comparing energy required to recover one mole of solvent from binary mixtures using each separation method vs. $CED_{incin.}$ → the least energy intensive end-of-life route.

- The separation of binary mixtures are based on **the recovery of one mixture component** at 99.5% (virgin) purity.
- The **recovered solvent** must be that which **permeates** using OSRO; the actual calculated distillation Q_{min} must be halved.
- Further work must be done for OSRO **retentate recovery**.

Table 2. Solvents in binary mixtures and recovered solvent

Ref Solvent: IPA	Methanol	Toluene	Cyclohexanone
Recovered Solvent	*Methanol*	*IPA*	*IPA*

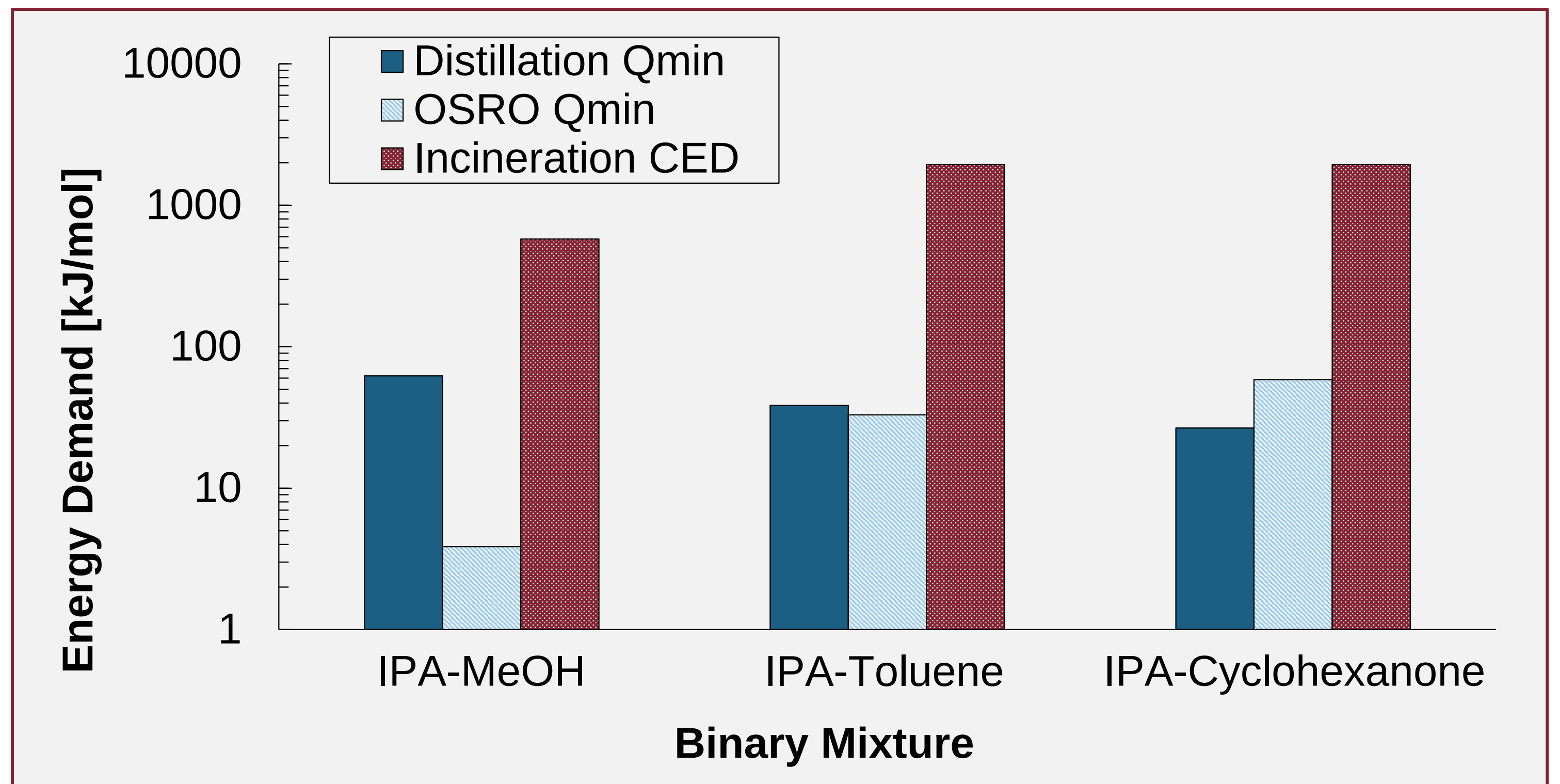


Fig. 9. End-of-life processing routes have energy demands that **differ due to components** present in mixture

Conclusion

- **Distillation** Q_{min} is dependent on the difference in T_b between the solvents in the binary mixture and recovers both solvents.
- **OSRO** requires stages, and Q_{min} depends on the polarity, viscosity, and size of the solvents, recovering the permeate.
- Larger molecules have higher Q returns when **incinerated**.
- In example, OSRO is the **least energetically demanding** end-of-life process for the IPA-methanol and IPA-toluene mixtures, while distillation is preferred for IPA-cyclohexanone.

References

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