Supporting Information

Assigning Chemical and Process Safety Index scores

Heat of the reaction subindices I_{rm} and I_{rs}

Table S 1

Heat of reaction / total reaction mass / J / g	Score
Thermally neutral ≤ 200	0
Mildly exothermic < 600	1
Moderately exothermic < 1200	2
Strongly exothermic < 3000	3
Extremely exothermic ≥ 3000	4

Chemical interaction subindex I_{int} :

Table S 2

Chemical Interaction	Score
Heat formation	1 - 3
Fire	4
Formation of harmless nonflammable gas	1
Formation of toxic gas	2 - 3
Formation of flammable gas	2 - 3
Explosion	4
Rapid polymerization	2 - 3
Soluble toxic chemicals	1

Flammability subindex I_{fl} :

Table S 3

Flammability	Score
Nonflammable	0
Combustible (flash point $> 55°C$)	1
Flammable (flash point $\leq 55°C$)	2
Easily flammable (flash point $< 21°C$)	3
Very flammable (flash point $< 0°C$ & boiling point $\leq 35°C$)	4

Explosiveness subindex I_{ex} **:**

Table S 4

Explosiveness (UEL-LEL) / *vol%*	Score
nonexplosive	0
0 ✍20	1
20 ✍45	2
45 ✍70	3
70 ✍100	4

Toxicity subindex $\boldsymbol{I_{tox}}$ **:**

Table S 5

Toxic limit / *ppm*	Score
TLV > 10000	0
TLV ≤ 10000	1
TLV ≤ 1000	2
TLV ≤ 100	3
TLV ≤ 10	4
TLV ≤ 1	5
TLV ≤ 0.1	6

Corrosivness subindex I_{cor} **:**

Table S 6

Construction material required	Score
Carbon steel	0
Stainless steel	1
Better material needed	2

Process Inventory subindex I_i :

Table S 7

Inventory		
ISBL /tones or kg	OSBL /tones or kg	Score
$0-1$	$0-10$	0
$1-10$	$10-100$	1
$10-50$	$100-500$	2
$50-200$	$500-2000$	3
$200-500$	$2000-5000$	4
$500-1000$	$5000-10000$	5

Process Temperature subindex I_t :

Table S 8

Process Temperature / °C	Score
< 0	1
$0-70$	0
$70-150$	1
$150-300$	2
$300-600$	3
> 600	4

Process Pressure subindex I_p :

Table S 9

Pressure /bar	Score
$0.5-5$	0
$0-25$ or $5-25$	1
$25-50$	2
$50-200$	3
$200-1000$	4

Equipment safety index I_{Isbl} and I_{Osbl} :

Table S 10

Equipment	Score I_{Isbl}
Equipment handling nonflammable, nontoxic materials	0
Heat exchangers, pumps, towers and drums	1
Air coolers, reactors, high hazard pumps	2
Compressors, high hazard reactors	3
Furnaces, fired heaters	4

Table S 11

Equipment	Score I_{Osbl}
Equipment handling nonflammable, nontoxic materials	0
Atmospheric storage tanks, pumps	1
Cooling towers, compressors, blowdown systems	2
Flares, boilers, furnaces	3

Process structure index I_{st} :

Table S 12

Safety level of process structure	Score
Recommended (safety etc. standard)	0
Sound engineering practice	1
No data or neutral	2
Probably unsafe	3
Minor accidents	4
Major accidents	5

WAR Algorithm and determination of its parameters

The WAR algorithm calculates the overall potential environmental impact, Ψ_k of chemical k using the following equation.

$$\Psi_k = \sum_l \alpha_l \psi_{kl}^s$$

where,

l is the impact category.

α_l is the relative weighing factor for impact category l.

ψ_{kl}^s is the specific potential environment impact for chemical k for category l.

A. Impact Categories and their scores:

1. Human toxicity potential by ingestion (HTPI): This is determined by using values for lethal-dose that causes death in 50% of rats by oral ingestion (LD_{50}).

$$(Score)_{k,HTPI} = \frac{1}{(LD_{50})_k}$$

2. Human toxicity potential by exposure both dermal and inhalation (HTPE): This is estimated using time weighted average values of the threshold limit values $(TLV)_{\text{time}}$ for exposure to chemicals as published by OSHA, ACGIH and NIOSH.

$$(Score)_{k.HTPE} = \frac{1}{(TLV)_{time}}$$

3. Terrestrial toxicity potential (TTP): This is determined similar to HTPI using LD_{50} data.

$$(Score)_{k,TTP} = \frac{1}{(LD_{50})_k}$$

4. Aquatic toxicity potential (ATP): ATP values are derived from LC_{50} (lethal concentration) which causes death in the fish species Pimephales promelas.

$$(Score)_{k,ATP} = \frac{1}{(LC_{50})_k}$$

5. Global warming potential (GWP): GWP is determined by calculating the amount of infrared radiation a given chemical absorbs over its atmospheric life time as compared to that of a reference compound usually CO_2 as shown in the equation below

$$(Score)_{k,GWP} = \frac{\int_0^{TH} a_k \cdot [k(t)]dt}{\int_0^{TH} a_{ref} \cdot [ref(t)]dt}$$

where TH is the time horizon taken as 100 years.

a_k and a_{ref} are radiative efficiencies, the increase in radiation absorption per unit increase in abundance of the chemical species and,

$[k(t)]$ and $[ref(t)]$ are the time dependent decay in abundance.

6. Ozone depletion potential (ODP): ODP is defined as the ratio of the rate at which a unit mass of chemical reacts with ozone to produce molecular oxygen to the rate at which a unit mass of CFC-11(trichlorofluoromethane) reacts with ozone.

$$(Score)_{k,ODP} = \frac{rate_k}{rate_{CFC-11}}$$

7. Photochemical oxidation potential (PCOP): PCOP, also known as smog formation potential is the ratio of the rate at which a chemical reacts with a hydroxyl radical ($OH^{\cdot}$) to that of the rate of reaction of ethylene with $OH^{\cdot}$.

$$(Score)_{k,PCOP} = \frac{rate_k}{rate_{ethylene}}$$

8. Acidification potential (AP): AP or acid rain potential is the ratio of rate at which a chemical reacts with moisture to release H^+ in the atmosphere to the rate of at which sulphur dioxide(SO_2) reacts to produce H^+.

$$(Score)_{k,AP} = \frac{rate_k}{rate_{SO_2}}$$

B. Weighing factor:

The weighing factor α_l gives user defined weights to each of the eight impact potentials and is usually assigned on a scale of 0 to10.

C. Specific potential environment impact ψ_{kl}^{s} : The individual scores are normalized within their categories to give the specific PEI for that chemical

$$\psi_{kl}^{s} = \frac{(Score)_{kl}}{\langle (Score)_{k} \rangle_{l}}$$

where $(Score)_{kl}$ represents the scores for impacts on their respective scales and, $\langle (Score)_{k} \rangle_{l}$ is the average value of all chemicals in impact category l .

Input Data for WAR Algorithm:

1) Silica Lab

Table S 13: Input Data for Sol Gel synthesis

Stream Name	Reaction	Washing	Waste	Product
Type	Inlet	Inlet	Outlet Waste	Product
Flow Rate*	3.50E ✍01	3.58E ✍01	7.06E ✍01	7.00E ✍04
X(Ethanol)	0.9027	0.4400	0.6657	0.0000
X(Ammonia)	0.0873	0.0000	0.0482	0.0000
X(TEOS)	0.0100	0.0000	0.0000	0.0000
X(Water)	0.0000	0.5600	0.2833	0.0000
X(Silicon Dioxide)	0.0000	0.0000	0.0028	1.0000

2) Flame-TEOS

Table S 14: Input Data for Flame Synthesis using TEOS

Stream Name	TEOS-Ar	Argon	Hydrogen	Oxygen	Air	Product	Waste
Type	Inlet	Inlet	Inlet	Inlet	Inlet	Product	Waste
Flow Rate	3.14E−01	1.06E ✍01	3.21E ✍02	1.29E ⊟00	4.93E ⊟00	6.00E ✍02	6.32E ⊟00
X(TEOS)	0.6600	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
X(Argon)	0.3400	1.0000	0.0000	0.0000	0.0000	0.0000	0.0340
X(Hydrogen)	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
X(Oxygen)	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.1020
X(Air)	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.7810
X(Carbon Dioxide)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0550
X(Water)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0280
X(Silicon Dioxide)	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000

3) Flame-HMDSO

Table S 15: Input Data for Flame Synthesis using HMDSO

Name	Argon	Methane	Oxygen	Waste Gas	Product
Type	Inlet	Inlet	Inlet	Outlet Waste	Product
Flow Rate	6.30E ✍02	2.00E ✍02	4.80E ✍01	3.22E ✍01	2.50E ✍02
X(Silicon Dioxide)	0.0000	0.0000	0.0000	0.0000	1.0000
X(Argon)	0.4700	0.0000	0.0000	0.0928	0.0000
X(Methane)	0.0000	1.0000	0.0000	0.0000	0.0000
X(Oxygen)	0.0000	0.0000	1.0000	0.5582	0.0000
X(Carbon Dioxide)	0.0000	0.0000	0.0000	0.3490	0.0000
X(HMDSO)	0.5300	0.0000	0.0000	0.0000	0.0000

4) Weighting profile: The following weights were used for the three method

Table S 16

Category	HTPI	HTPE	TTP	ATP	GWP	ODP	PCOP	AP
Weight	1	1	1	1	1	1	1	1

5) Product streams and Energy usage were not included in the calculations.

NAIADE CALCULATIONS:

Tables S17-S22 depict the steps involved in the NAIADE calculations namely, determining the semantic distance, pairwise comparison of alternatives, preference intensity index and the corresponding entropy.

The three processes are labeled as following,

A. Sol-Gel Synthesis.

B. Flame TEOS

C. Flame HMDSO

Table S 17: Semantic distance from pairwise comparison

Parameters	(A,B)		(A,C)		(B,C)	
	Expected Value Difference	Semantic Distance	Expected Value Difference	Semantic Distance	Expected Value Difference	Semantic Distance
Yield	-59.3	-59.3	-24.3	-24.3	-35.0	-35.0
Particle Size	-0.3000	0.2940	-0.2000	0.2026	0.1000	0.1303
Cost per unit	34.94	34.94	35.04	35.04	0.10	0.10
Chemical Safety Index	-11.0	-11.0	-4.0	-4.0	7.0	7.0
Process Safety Index	-4	-4	-3	-3	1	1
Material Procurement	627.3	627.3	715.88	715.88	88.58	88.58
Generation of Waste	899.0	899.0	991.12	991.12	92.12	92.12
Hazardous Material	0.2537	0.2406	0.1537	0.1550	-0.1000	0.1222
% Atom Economy	-1.1010	-1.1010	-2.4400	-2.4400	-3.5410	-3.5410
Solvent Index	0.0791	0.0791	0.0791	0.0791	0.0000	0.0000
PEI	869.9979	869.9979	869.9984	869.9984	0.0005	0.0005

Table S 18: Preference Relation Functions between Alternatives A and B

(A,B)	$\mu_{>>}$	$\mu_{>}$	$\mu_{\cong}$	$\mu_{==}$	$\mu_{<}$	$\mu_{<<}$
Yield	0.0000	0.0000	0.0000	0.0000	0.9974	0.9962
Particle Size	0.0000	0.0000	0.3211	0.0000	0.5902	0.3763
Cost per unit	0.0000	0.0000	0.0000	0.0000	0.9927	0.9892
Chemical Safety Index	0.8988	0.9308	0.0221	0.0000	0.0000	0.0000
Process Safety Index	0.5000	0.6400	0.2500	0.0000	0.0000	0.0000
Material Procurement	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Generation of Waste	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000

Hazardous Material	0.0000	0.0000	0.3946	0.0009	0.5074	0.2827
% Atom Economy	0.0239	0.1187	0.6828	0.4316	0.0000	0.0000
Solvent Index	0.0000	0.0000	0.9730	0.9957	0.0007	0.0000
PEI	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000

Table S 19: Preference Relation Functions between Alternatives A and C

(A,C)	$\mu_{>>}$	$\mu_{>}$	$\mu_{\cong}$	$\mu_{==}$	$\mu_{<}$	$\mu_{<<}$
Yield	0.0000	0.0000	0.0002	0.0000	0.9850	0.9779
Particle Size	0.0000	0.0000	0.4734	0.0106	0.3902	0.1711
Cost per unit	0.0000	0.0000	0.0000	0.0000	0.9927	0.9893
Chemical Safety Index	0.5000	0.6400	0.2500	0.0000	0.0000	0.0000
Process Safety Index	0.3317	0.5000	0.3536	0.0020	0.0000	0.0000
Material Procurement	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Generation of Waste	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000
Hazardous Material	0.0000	0.0000	0.5862	0.0981	0.2744	0.0866
% Atom Economy	0.0000	0.0000	0.4293	0.0161	0.3981	0.2239
Solvent Index	0.0000	0.0000	0.9730	0.9957	0.0007	0.0000
PEI	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000

Table S 20: Preference Relation Functions between Alternatives B and C

(B,C)	$\mu_{>>}$	$\mu_{>}$	$\mu_{\cong}$	$\mu_{==}$	$\mu_{<}$	$\mu_{<<}$
Yield	0.9893	0.9927	0.0000	0.0000	0.0000	0.0000
Particle Size	0.0225	0.1379	0.6256	0.1668	0.0000	0.0000

Cost per unit	0.0000	0.0000	0.9659	0.9931	0.0011	0.0000
Chemical Safety Index	0.0000	0.0000	0.0884	0.0000	0.8448	0.7759
Process Safety Index	0.0000	0.0000	0.7071	0.5000	0.1000	0.0172
Material Procurement	0.0000	0.0000	0.0000	0.0000	0.9989	0.9983
Generation of Waste	0.0000	0.0000	0.0000	0.0000	0.9989	0.9984
Hazardous Material	0.0225	0.1379	0.6119	0.1403	0.0000	0.0000
% Atom Economy	0.0000	0.0000	0.2931	0.0002	0.5821	0.4280
Solvent Index	0.0000	0.0000	1.0000	1.0000	0.0000	0.0000
PEI	0.0000	0.0000	0.9998	1.0000	0.0000	0.0000

Table S 21: Preference Intensity Indices between Alternatives after Aggregation.

Aggregation of Criteria	$\mu_{>>}$	$\mu_{>}$	$\mu_{\cong}$	$\mu_{==}$	$\mu_{<}$	$\mu_{<<}$
(A,B)	0.1434	0.1813	0.2468	0.1484	0.6727	0.6317
(A,C)	0.0265	0.0863	0.2818	0.1333	0.6902	0.6073
(B,C)	0.1297	0.1373	0.6080	0.4316	0.4034	0.3652

Table S22: Entropy Level Associated with the Preference Intensity Indices.

Entropy	$H_{>>}$	$H_{>}$	$H_{\cong}$	$H_{==}$	$H_{<}$	$H_{<<}$
(A,B)	0.1339	0.1187	0.0982	0.0933	0.1877	0.0112
(A,C)	0.0909	0.1766	0.2856	0.0037	0.0159	0.0218
(B,C)	0.0078	0.0057	0.2733	0.0963	0.1480	0.1625