

A large, white, cylindrical industrial storage tank is the central focus of the image. The tank is surrounded by a complex network of pipes, ladders, and walkways. The pipes are primarily white and grey, with some red and blue sections. The ladders and walkways are made of metal and have yellow safety railings. The tank is situated in an industrial facility, with other structures and equipment visible in the background. The sky is blue with some light clouds. The overall scene is a detailed view of an industrial storage and processing area.

**VOC EMISSION
MINIMIZATION**

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1.0 MANAGEMENT SUMMARY

This report reviews the implications of using a wet scrubbing process to remove VOC components at infinite dilution from extract air arising from paint booth operations. CHEMCAD Version 5.1 process modelling and dynamic simulation software has been used throughout this report. VOC solubility in water systems have been studied using Raschig WINSORP Version 4.5 proprietary software.

Process Thermodynamics (Section 3.0)

To make accurate component behaviour and performance predictions the use of an appropriate thermodynamic model is paramount. Infinite dilution system behaviour is difficult to predict and the results presented can only be considered as an order of magnitude accurate. This study has only considered single component scenarios; multi-component behaviour can vary appreciably. However the behaviour predicted does enable reasonable conclusions to be made concerning the performance and operational difficulties associated with the proposed system. If it is intended to proceed further with the intention to install a system of this type it is strongly recommended that the system behaviour be validated by experimental study and any proposed supplier be required to provide adequate data with suitable process guarantee.

Choice of Scrubbing Liquor (Section 4.2)

Scrubbing liquors proposed included propylene glycol, diesel and vegetable oils.

The vapour liquid equilibrium process model indicates that the contribution to atmospheric VOC emission is unacceptable with propylene glycol or diesel as the air flow strips VOCs from these liquors.

A typical vegetable oil composition (Appendix II) was used to study the proposed process. The physical properties of the primary components in vegetable oils demonstrate poor hydraulic properties for use as scrubbing liquids namely relatively high viscosity and freezing point. The selection of the circulating oil will require careful consideration as to its operational suitability as a scrubbing liquid in order to provide adequate wetting of the packing and freeze protection.

Performance Prediction (Section 5.0)

On the basis of fresh scrubbing liquor being used (ie no recirculation), the key components N-Butanol, O-Xylene and MIBK demonstrate adequate vapour liquid equilibrium properties to satisfy the consent limits using a four theoretical stage scrubbing process. However sourcing a vegetable oil exhibiting suitable hydraulic properties will be cause for concern.

As soon as recirculation is introduced the consent limits are exceeded in less than two hours when using a 20 m³ capacity liquor tank. However if facilities could be provided to facilitate removal of dissolved VOC from the circulation liquor then a satisfactory process could be achieved.

2.0 PROPOSED PROCESS SPECIFICATION

The plant comprises spray booths exhausting at a maximum airflow rate of 72,700 m³/h, reference 15°C. This is achieved using an exhaust air fan with a variable speed drive adjusting the air flow depending on the number of booths operating at any one time.

VOC contamination can be any or all of the following components at varying composition mixes depending on what is being tested. Component mixtures can consist of the following with n-butanol, MIBK and xylene being the most predominant:-

White Spirit,

Alcohols including n-butanol, methanol

Ketones including Xylene, Styrene(vinyl benzene), MIBK

Inlet concentrations, as total VOC, can be up to 550 mg/m³ which is the design point.

The design outlet concentration has been set at 50 mg/m³ although the consent level will be 100 mg/m³ with volume referenced to 15°C.

A packing height of 6m maximum has been proposed, based on using fresh scrubbing liquor being used ie no dissolved VOCs present. However, no correlation has been established as to what levels the contaminants can be allowed to build up in the recirculating liquor before replacement is required.

This report investigates the solubility characteristics of the key components and considers the worst case scenarios to establish the operational constraints.

Scrubbing liquors being considered are propylene glycol and vegetable oil (unspecified). Diesel oil is also to receive consideration.

This report has been based on the following scrubber design specification summary:

Air flow maximum	72,700 m ³ /h @ 15°C 1.01325 bar
Density	1.2205 kg/m ³
Maximum mass flow	88732 kg/h
Maximum inlet conc.	550 mg/m ³ (=40.00 kg/h)
Design outlet conc.	50 mg/m ³ (=3.635 kg/h)
Allowable outlet conc.	100 mg/m ³ (=7.27 kg/h)

The liquor flow has been based on a nominal 20000 kg/h. However this parameter has no bearing on the report conclusions re operability and liquor replacement strategy. Vegetable oil density of 900 kg/m³ gives volumetric flow of 22.18 m³/h.

3.0 PROCESS THERMODYNAMIC CONSIDERATIONS

The thermodynamic properties of infinitely dilute solutions is acknowledged as being very difficult to predict and systems involving these conditions should always have the results from process simulation work validated by experimental data.

The Predictive Soave Redlich Kwong (PSRK) equation is a group contribution equation-of-state which combines the SRK and UNIFAC models. This concept makes use of recent developments and has the main advantage that vapour-liquid-equilibrium (VLE) can be predicted for a large number of systems without introducing new model parameters that must be fitted to experimental VLE data. The PSRK equation of state can be used for VLE predictions over a much larger temperature and pressure range than the UNIFAC approach and is easily extended to mixtures containing supercritical compounds. Additional PSRK parameters, including light gases, allows the calculation of gas/gas and gas/ alkane phase equilibrium.

The modified UNIFAC model (Dortmund) introduces temperature dependent interaction parameters. This allows a more reliable description of phase behaviour as a function of temperature. The modified UNIFAC (Dortmund) method also uses van der Waals (Q and R) properties which are slightly different than those used in the original UNIFAC method. The main advantages of the modified UNIFAC method are a better description of the temperature dependence and the real behaviour in the dilute region and that it can be applied more reliably for systems involving molecules very different in size.

The physical properties for vegetable oils are shown in Appendix II.

The boiling point curves for petroleum diesel and white spirit, which have been used in this study, are shown in Appendix III.

4.0 VOC SOLUBILITY BEHAVIOUR

4.1 Water

Henry's law applies to dilute aqueous solutions. It should not be applied to predict equilibrium partition coefficients between other liquid solutions and air, e.g., gasoline or oil. Instead, a number of other approximations have been developed to estimate liquid-air partition coefficients for non-aqueous solutions.

VOC Solubility in Water Data (Ref: Smallwood, Solvent Recovery)						
Solvent	Solubility in Water 25 °C % w/w	γ°	P mmHg 25 °C	$\gamma^\circ P$	H bar 25 °C (WINSORP)	H bar 15 °C (WINSORP)
methanol	totally miscible	2.2	127	279	0.356	0.2108
n-butanol	7.3	52.3	6.5	340	0.390	0.1702
ethyl acetate	7.7	45.8	94.6	4330	10.1	5.026
butyl acetate	0.7	1016	11.3	11500	15.0	7.958
xylene	0.02	29733	8.8	261000	271.0	164.1
MIBK	1.7		19.4			
methyl acrylate	5.7 ^{20°C}		88.2			
ethyl acrylate	1.48		39.4			
styrene	< 1.0		6.3			

Henry's Law Coefficient $H = \gamma P$ where P is the partial pressure, normally taken at 25°C. Deviation from ideal behaviour is predicted using the dimensional activity coefficient γ of the dissolved solvent in water. The design criteria for an economic air stripping process from water is $\gamma^\circ P > 250000$ which indicates that the removal of xylenes by absorption in water is impractical.

Raschig WINSORP software was used to check the suitability of water as a scrubbing liquid. As can be seen from the table of results below a practical solution is available for the scrubbing of the alcohols but is impractical for the esters and xylene.

Raschig WINSORP Version 4.5 Sizing Runs with 90 mm Raschig Plastic Pall Rings Basis: Column Diameter 3000 mm, Water Circulation 20 m ³ /h, VOC In 500 mg/m ³ , VOC Out 100mg/m ³								
Solvent	Min Liquor Flow (m ³ /h)	D_g m ² /s	D_l m ² /s	NTU	HETP m	H m	ΔP mbar	Loading %
methanol	9.15	1.50E-05	1.56E-09	1.79	1.81	3.23	10.3	52.4
n-butanol	7.39	8.35E-06	8.78E-10	1.49	2.8	4.16	13.26	52.4
ethyl acetate	218.5	8.11E-06	8.66E-10	15.67	1.51	23.66	148.04	83.4
butyl acetate	346.00	6.73E-06	7.04E-10	13.51	1.5	20.2	236.06	91.3
xylene	7134.7	6.84E-06	7.51E-10					

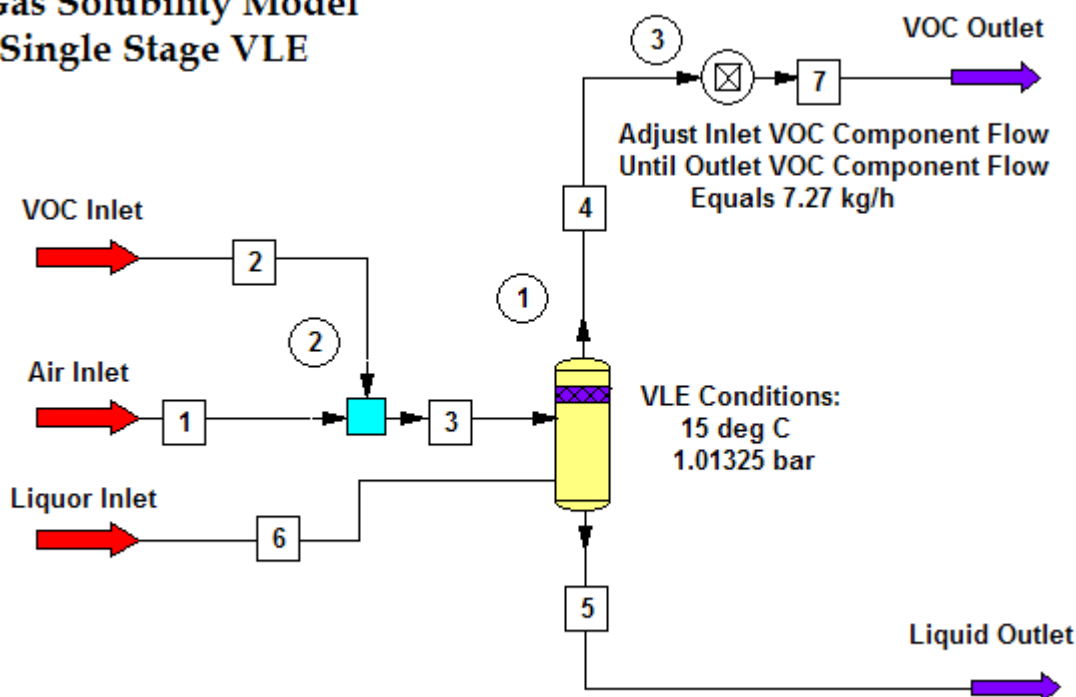
The sensitivity to dissolved VOC in the recirculating liquors was tested with the results being shown in the table below. The maximum concentration being limited by the packed height available nominally set at 6 m.

Raschig WINSORP Version 4.5 Sizing Runs with 90 mm Raschig Plastic Pall Rings Basis: Column Diameter 3000 mm, Water Circulation 20 m ³ /h, VOC In 500 mg/m ³ , VOC Out 100mg/m ³							
Solvent	Min Liquor Flow (m ³ /h)	Max Recirculation Inlet Composition mg/l	NT U	HETP m	H m	ΔP mbar	Loading %
methanol	10.59	440	3.32	1.81	6.00	19.12	52.4
n-butanol	7.39	400	2.16	2.8	6.05	19.28	52.4

4.2 Liquors under Consideration

VOC solubility behaviour was predicted using the CHEMCAD vapour liquid equilibrium model shown below. The fresh liquor rate was set at 20000 kg/h and individual component VOC species flows were adjusted until the outlet VOC composition met the consent limit. In the case of white spirit a single component was adjusted until the consent limit for total VOC was reached. This approach determines the maximum allowable VOC inlet concentration for an individual species and the VOC concentration in solution based on a single theoretical stage.

Gas Solubility Model Single Stage VLE



Vegetable Oil Single Stage Equilibrium Conditions at 15°C

Solvent	Modified UNIFAC		PSRK	
	Inlet (mg/m ³)	Solubility (kg/m ³)	Inlet (mg/m ³)	Solubility (kg/m ³)
methanol	90.16	0.033	85.88	0.016
n-butanol	279.27	0.790	430.51	1.395
ethyl acetate	99.9	0.072	98.95	0.068
butyl acetate	258.87	0.708	260.94	0.716
xylene	490.47	1.635	424.65	1.371
MIBK	188.66	0.427	218.97	0.548
methyl acrylate	120.48	0.154	102.11	0.081
ethyl acrylate	171.64	0.359	131.07	0.197
styrene	585.36	2.014	321.64	0.959
white spirit	198.8	0.468	188.21	0.465

It can be seen from the above that PSRK gives the more conservative (ie safe) predictions with the exceptions of n-butanol and MIBK components.

4.2 *Liquors under Consideration*

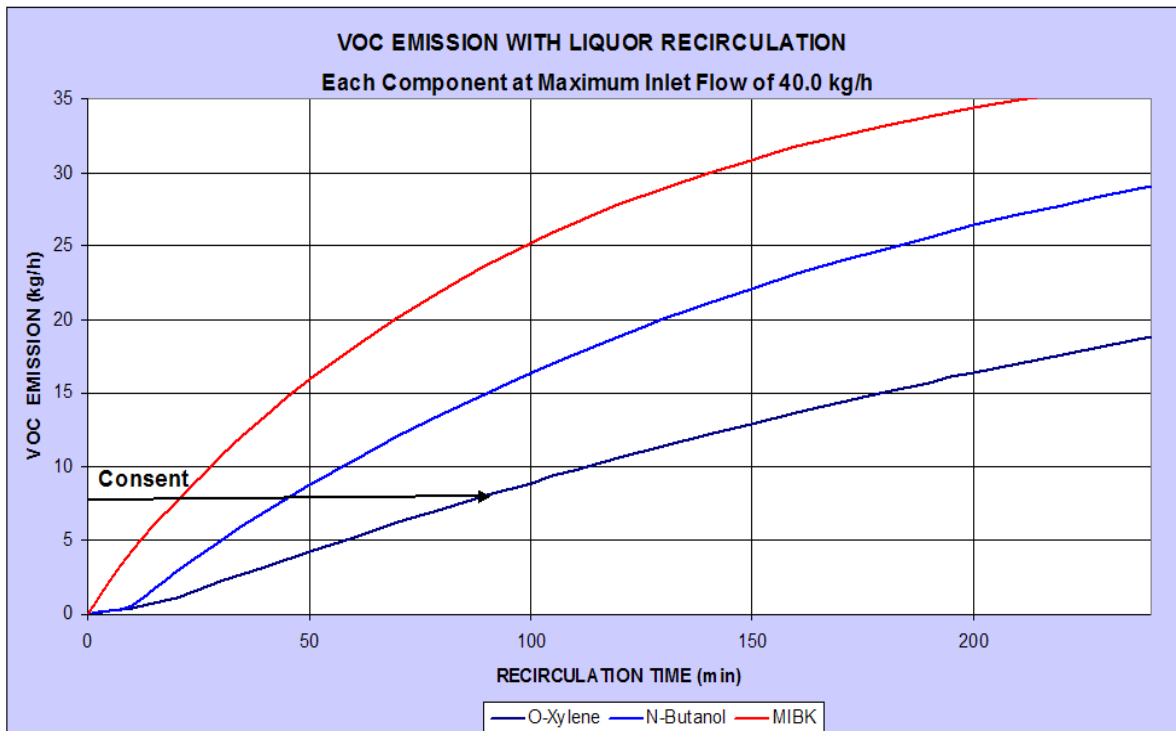
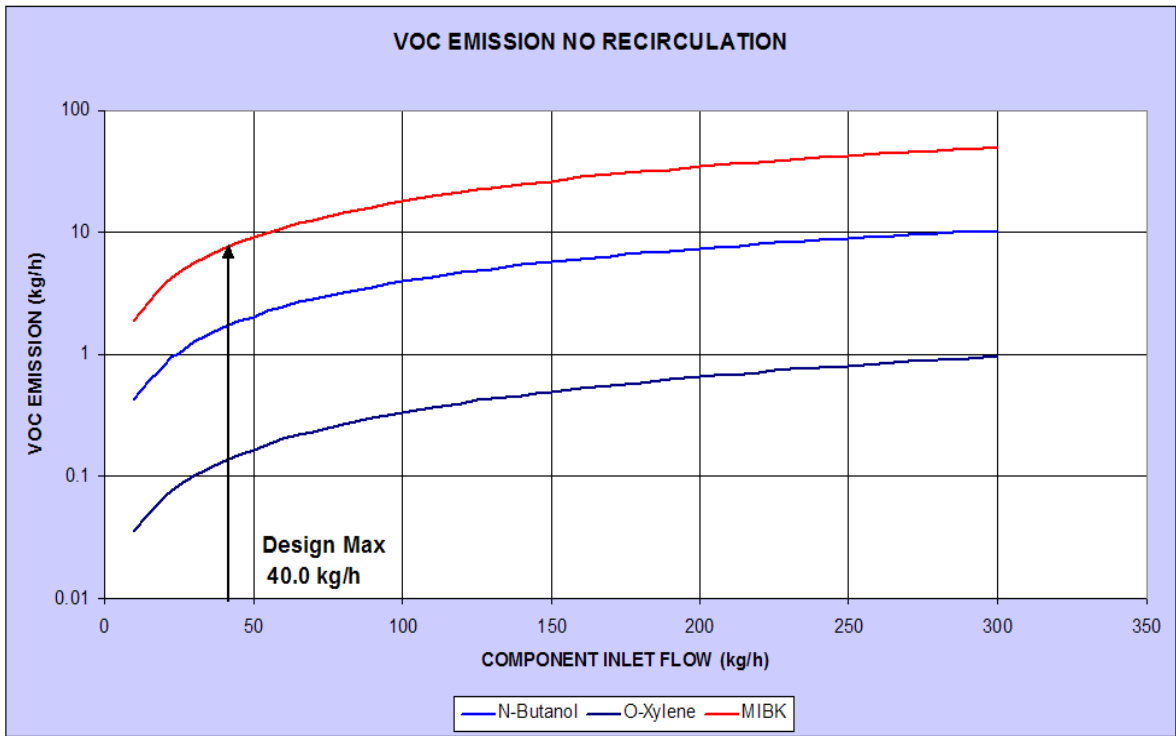
Propylene glycol properties are shown in the table below. However modified UNIFAC predicts that 15.16 kg/h and PSRK predicts 1.94 kg/h of propylene glycol will be stripped by the air to atmosphere.

propylene glycol Single Stage Equilibrium Conditions at 15°C				
Solvent	Modified UNIFAC		PSRK	
	Inlet (mg/m ³)	Solubility (kg/m ³)	Inlet (mg/m ³)	Solubility (kg/m ³)
methanol	185.16	0.413	157.55	0.303
n-butanol	802.75	2.884	1337.62	5.024
ethyl acetate	94.89	0.052	96.47	0.058
butyl acetate	141.32	0.238	159.69	0.311
xylene	148.2	0.265	181.45	0.398
MIBK	128.14	0.185	156.09	0.297
methyl acrylate	96.36	0.058	93.43	0.046
ethyl acrylate	104.81	0.092	102.22	0.081
styrene	130.51	0.194	122.17	0.161
white spirit	84.64	0.011	92.98	0.044

Diesel was evaluated based on a typical distillation curve shown in Appendix III. The outlet consent level of 100mg/m³ VOC is exceeded by the stripping effect of the air alone with modified UNIFAC predicting 285.9 mg/m³ and PSRK predicting 202.8 mg/m³ at 15°C making Diesel unsuitable for this application.

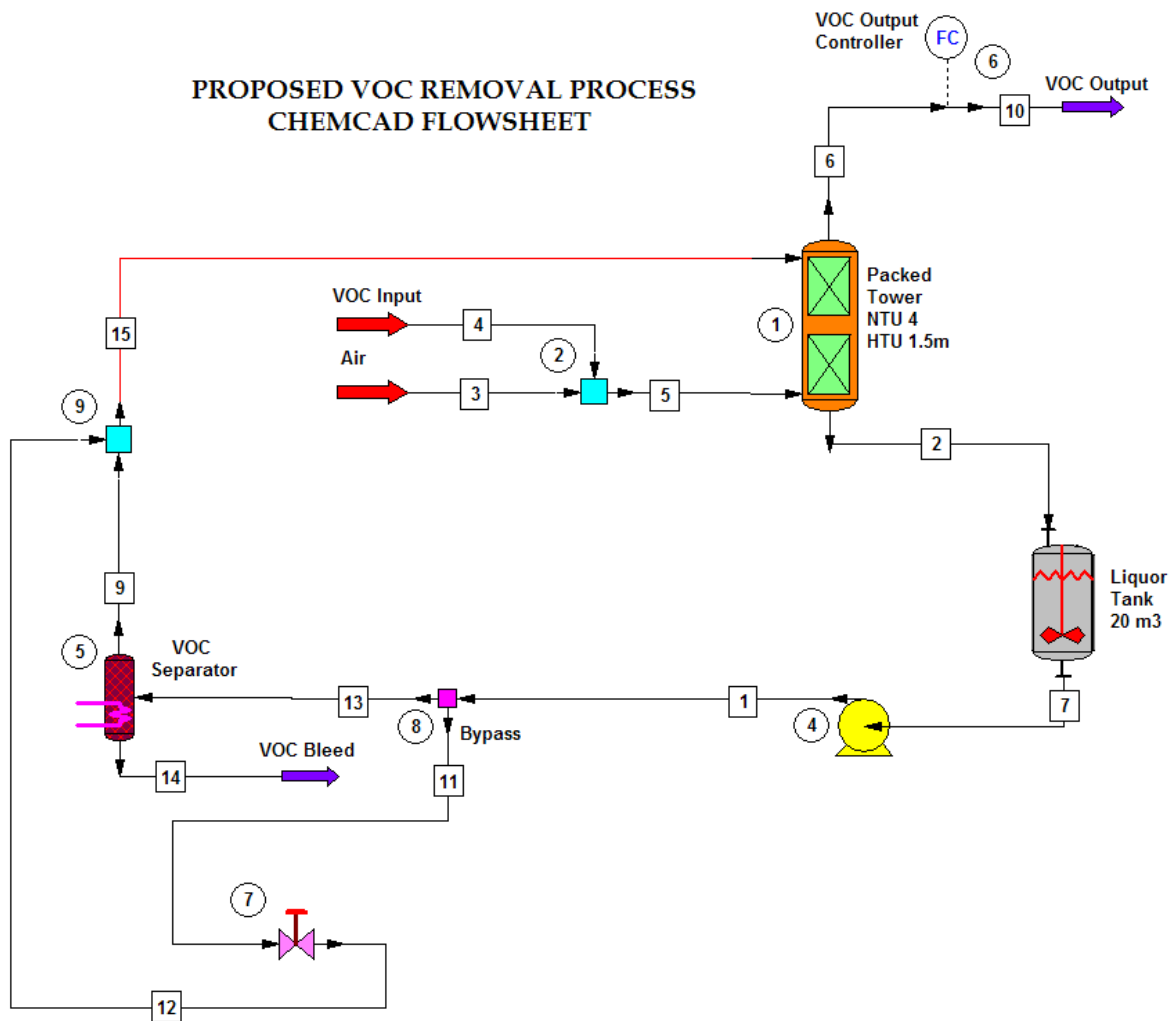
5.0 PROCESS PERFORMANCE PREDICTIONS

The performance predictions have been made using a regular vle model containing four theoretical stages. The air flow was set at the maximum design flow and the circulating liquor was vegetable oil at 20000kg/h. It can be seen that with no recirculation that the VOC emission to atmosphere is below the consent limit flow of 7.27 kg/h within the maximum design inlet single component flow of 40.0 kg/h for the key components N-butanol, O-Xylene and just over the limit with MIBK. As soon as recirculation is introduced the consent limit is exceeded within a relatively short time.



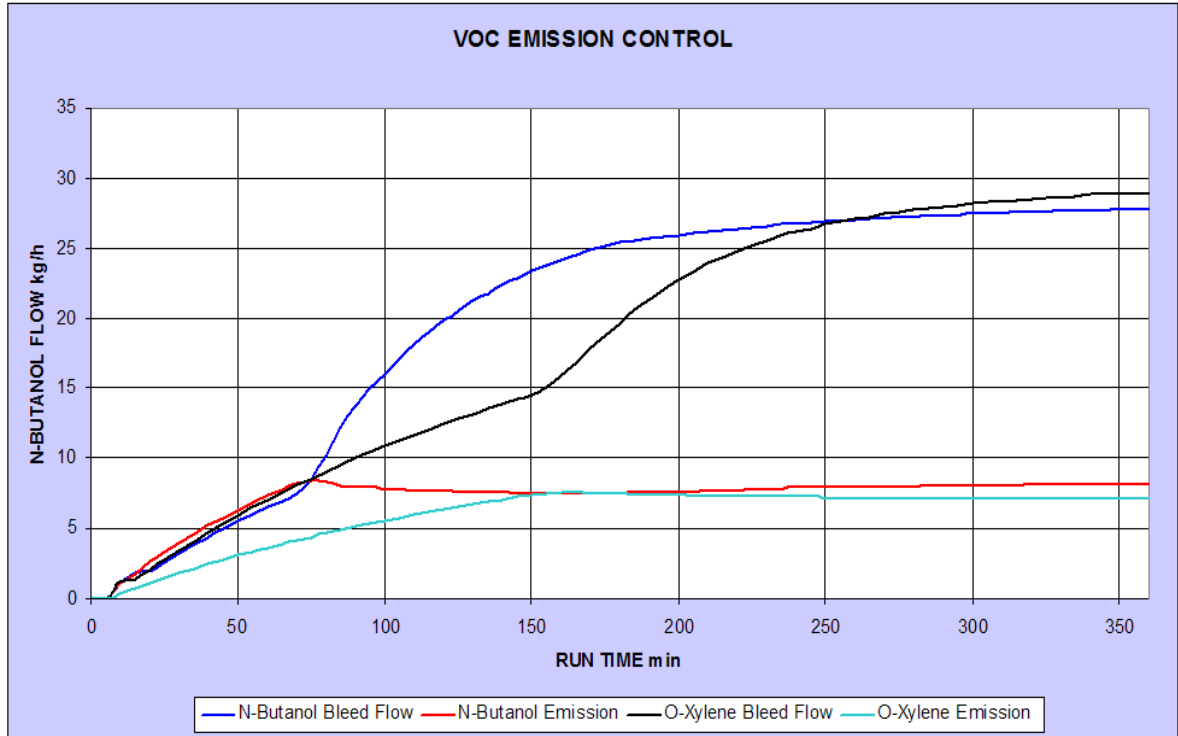
5.0 Process Performance Predictions

The CHEMCAD dynamic model, presented below, controls the VOC emission to atmosphere at the consent flow of 7.27 kg/h for the single component species under consideration by removing dissolved VOC from the system. The VOC input flow was set at 36.35 kg/h (500mg/m^3) based on the single component species under consideration with the air flow at maximum design of 88732 kg/h. The separator has a constant VOC bleed split ratio of 0.6 weight basis which applies throughout the simulation. The point at which the VOC bleed rate is increased to control the emission is where the emission curve kicks, namely at 70m for N-Butanol and 155m for O-Xylene.

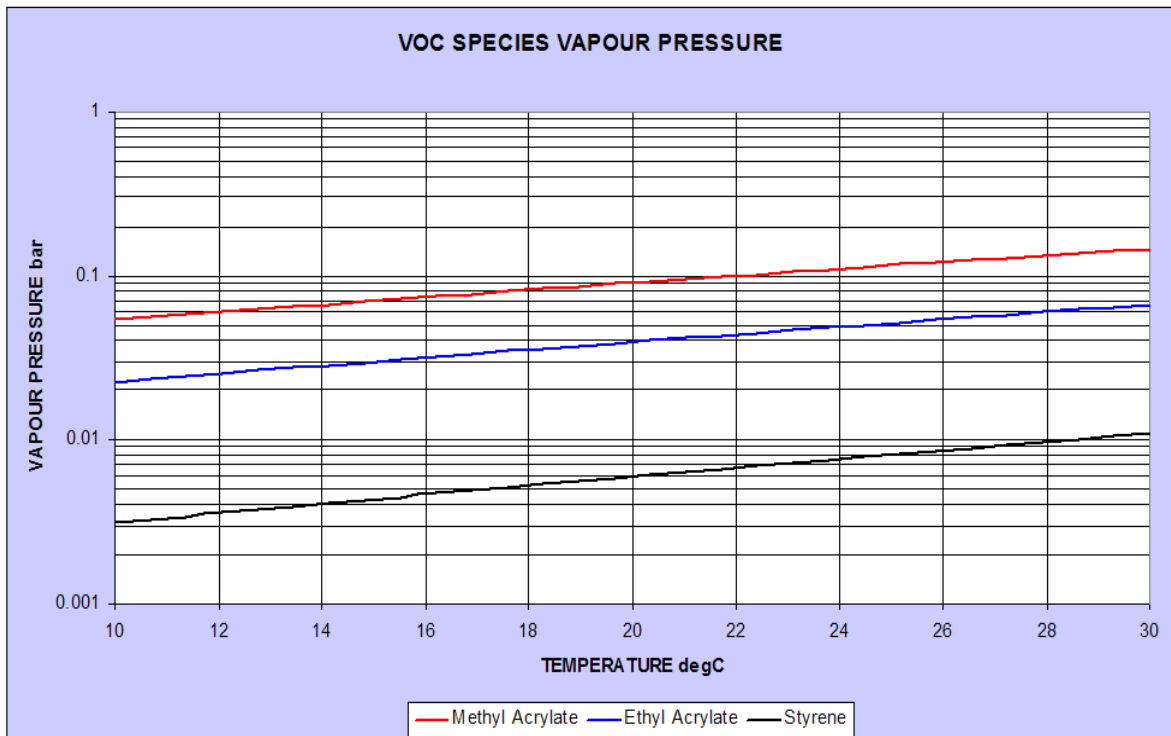
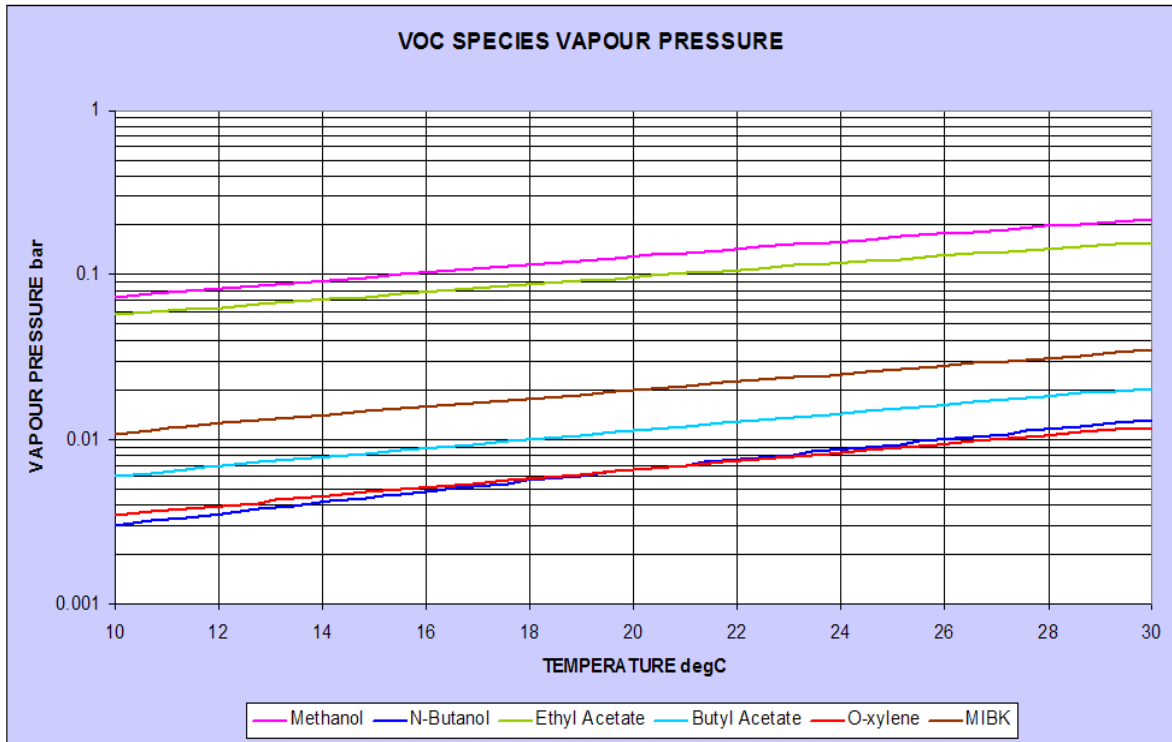


5.0 Process Performance Predictions

The dynamic simulation results shown in the curves below demonstrate that continuous recirculation without removal of some of the dissolved VOC will result in consent level non – compliance.



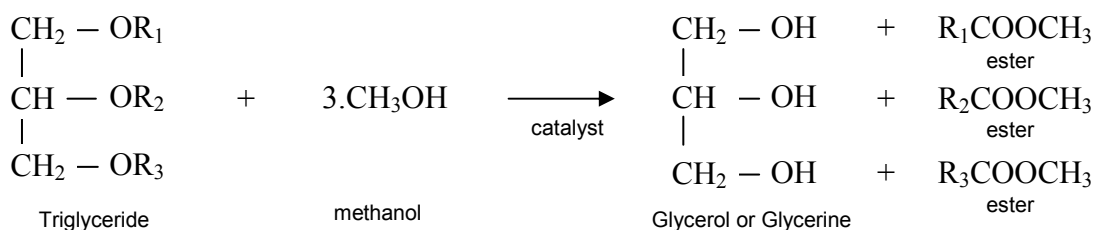
Appendix I VOC Species Property Data



Appendix II Vegetable Oils Property Data

Vegetable Oils

Vegetable oils are mainly liquid triglycerides, formed from one molecule of glycerol (glycerine) and three fatty acids, which may or not be the same fatty acid are catalytically reacted with methanol to give fatty esters, which are added to bio-diesel and glycerol.



where R_1 , R_2 and R_3 may be the same or different

Each oil contains different fatty acids and some examples are shown in the Table, below.

Examples of the structure of saturated, mono-unsaturated and poly-unsaturated (2 or more double bonds) fatty acids and their methyl esters are:-

Stearic acid – saturated also named octadecanoic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	$(\text{C}_{18}\text{H}_{36}\text{O}_2)$
methyl stearate	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$	$(\text{C}_{19}\text{H}_{38}\text{O}_2)$
Oleic acid – mono-unsaturated also named 9-octadecanoic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=(\text{CH}_2)_7\text{COOH}$	
methyl oleate	$\text{CH}_3(\text{CH}_2)_7\text{CH}=(\text{CH}_2)_7\text{COOCH}_3$	
Linoleic acid - poly-unsaturated also named 9, 12-octadecadienoic acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	$(\text{C}_{18}\text{H}_{31}\text{O}_2)$
methyl linoleate	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3$	

Appendix II Vegetable Oils Property Data

Fatty acid composition of some common edible fats and oils.

Percent by weight of total fatty acids.

Oil or Fat	Unsat./ Sat. ratio	Saturated					Mono unsaturated	Poly unsaturated	
		Capric Acid	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid	Oleic Acid	Linoleic Acid (ω6)	Alpha Linolenic Acid (ω3)
		C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3
Almond Oil	9.7	-	-	-	7	2	69	17	-
Beef Tallow	0.9	-	-	3	24	19	43	3	1
Butterfat (cow)	0.5	3	3	11	27	12	29	2	1
Butterfat (goat)	0.5	7	3	9	25	12	27	3	1
Butterfat (human)	1.0	2	5	8	25	8	35	9	1
Canola Oil (Rape seed)	15.7	-	-	-	4	2	62	22	10
Cocoa Butter	0.6	-	-	-	25	38	32	3	-
Cod Liver Oil	2.9	-	-	8	17	-	22	5	-
Coconut Oil	0.1	6	47	18	9	3	6	2	-
Corn Oil (Maize Oil)	6.7	-	-	-	11	2	28	58	1
Cottonseed Oil	2.8	-	-	1	22	3	19	54	1
Flaxseed Oil	9.0	-	-	-	3	7	21	16	53
Grape seed Oil	7.3	-	-	-	8	4	15	73	-
Lard (Pork fat)	1.2	-	-	2	26	14	44	10	-
Olive Oil	4.6	-	-	-	13	3	71	10	1
Palm Oil	1.0	-	-	1	45	4	40	10	-
Palm Olein	1.3	-	-	1	37	4	46	11	-
Palm Kernel Oil	0.2	4	48	16	8	3	15	2	-
Peanut Oil	4.0	-	-	-	11	2	48	32	-
Safflower Oil*	10.1	-	-	-	7	2	13	78	-
Sesame Oil	6.6	-	-	-	9	4	41	45	-
Soybean Oil	5.7	-	-	-	11	4	24	54	7
Sunflower Oil*	7.3	-	-	-	7	5	19	68	1
Walnut Oil	5.3	-	-	-	11	5	28	51	5

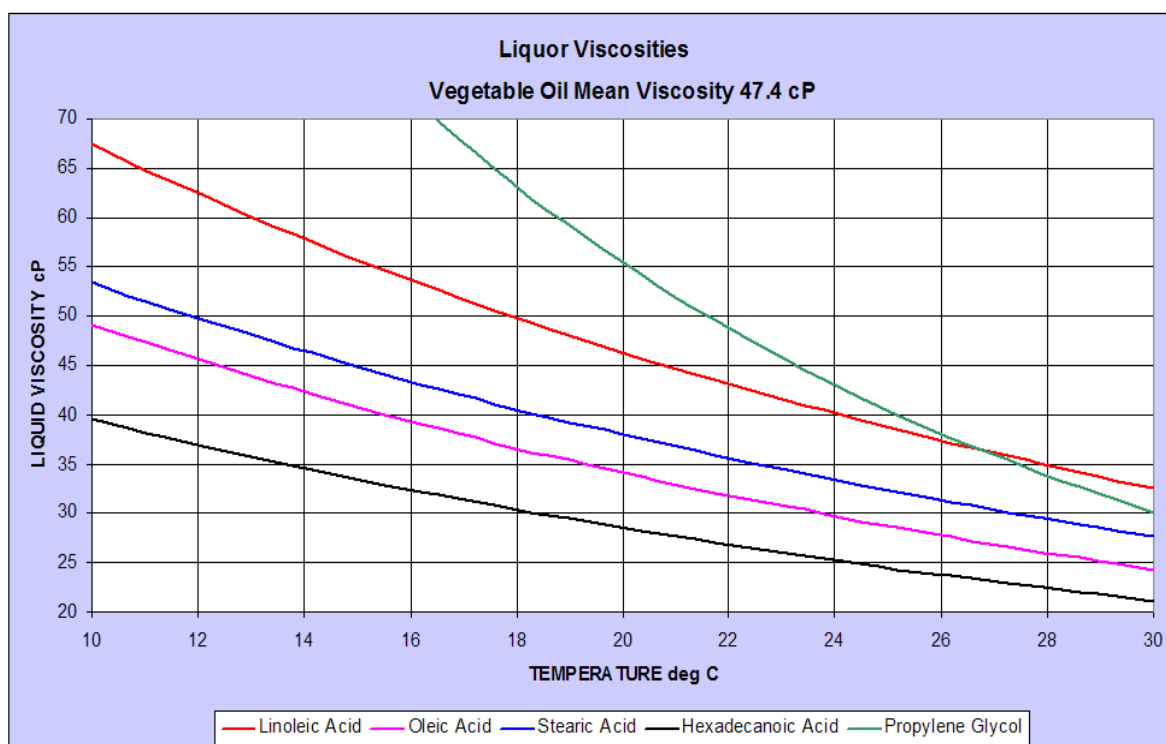
Percentages may not add up to 100% due to other constituents not listed

Appendix II Vegetable Oils Property Data

The vegetable oil composition used in this study is shown below and is similar to sunflower oil:

Component	CCD ID	Weight Fraction	MW kg/kmol	Boiling Pt °C	Freezing Pt °C
Linoleic Acid	548	0.64	280.45	354.85	-5
Oleic Acid	549	0.17	282.46	359.85	13.38
Stearic Acid	550	0.039	284.8	375.2	69.6
Hexadecanoic Acid	912	0.148	256.93	351	62.8
Mixture		1.00	277.1		11.89

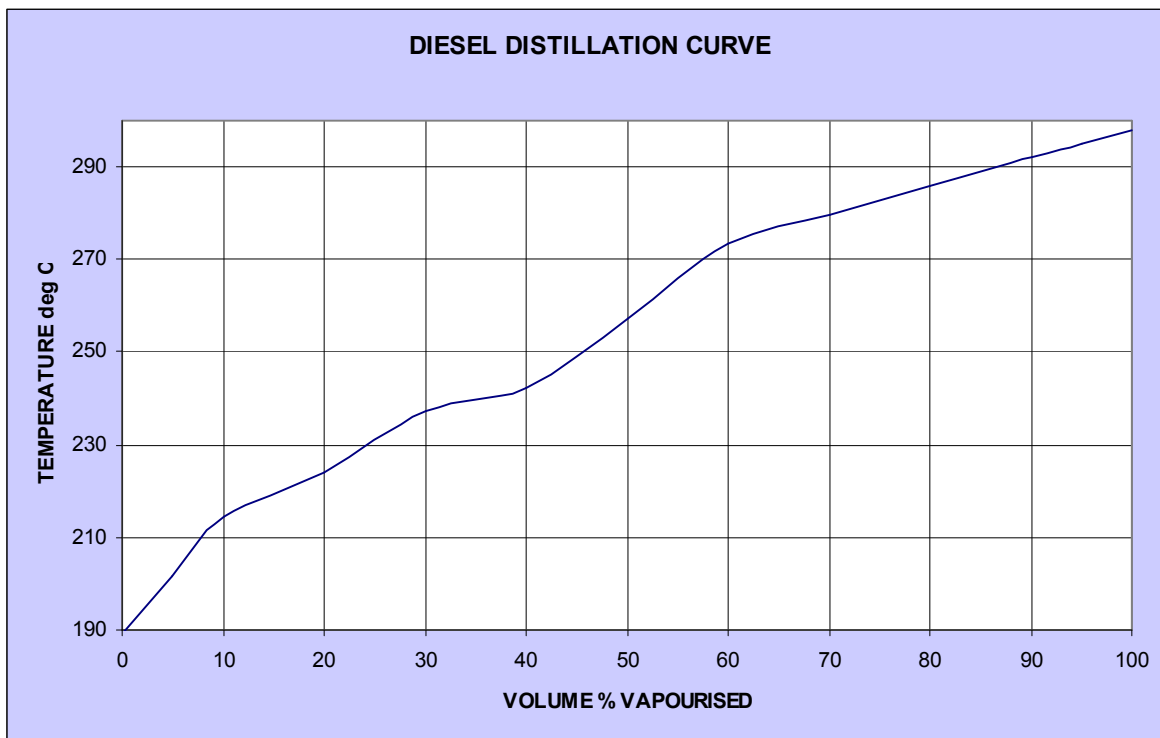
The viscosity of the main components of typical vegetable oils are shown in the graphs below. Propylene glycol has been shown for completeness.



The physical properties of propylene glycol and the main constituents in vegetable oils demonstrate poor properties for use as scrubbing liquids namely relatively high viscosities and freezing points. The selection of the circulating oil will require careful consideration as to its operational suitability as a scrubbing liquid to provide adequate wetting of the packing and freeze protection precautions.

Appendix III Hydrocarbon Property Data

#2 Diesel has a boiling point in the range 190°C to 325 °C and consists of a mixture of paraffins, aromatics, naphthalene (<2.9%), benzene (<0.09%) and sulphur (<0.49%). Typical API Gravity at 15.6 °C of 35.5° (SG 0.8473) and a viscosity 2.37 mm²/s (2 cps).



White spirit composition was based on the following species weight fractions:
n-hexane 0.025, n-heptane 0.175, n-octane 0.55, n-nonane 0.25

