TRUMPLER International

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Chemical Oxygen Demand: Fatliquors & Retanning Agents

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What is COD?

- **Chemical Oxygen Demand**
  - A direct quantification of the amount of **OXIDISABLE MATTER** present
    - Using potassium dichromate as the oxidant and a defined analytical method
  - An indirect indication of the amount of **ORGANIC MATTER** present
    - Expressed as mg O_2/L, ppm or kg O_2 per mass or area of product produced or starting material processed

- **Organic matter**
  - Compounds that contain carbon
    - Excludes simple oxides, carbonates, cyanides and carbides

A Reminder: Why is COD Important?

- **Reliability**
  - The current COD analytical method provides relatively consistant, reproduceable results without excessive cost or time
  - Widely accepted as the best general representation of the “polluting power” of an effluent and commonly utilised as a benchmark for
    - Effluent treatment plant efficiencies etc.
    - Charges, e.g., Mogden Formula (UK)

Charge for disposal (pence per m^3)= $R + \mathbf{V} + V_b + B \times \mathbf{Ot/Os} + S \times \mathbf{St/Ss}$

- R = Unit cost for conveyance (pence/cubic metre)
- V = Unit cost for volumetric treatment (pence/cubic metre)
- V_b = Additional volume charge if there is no biological treatment
- B = Unit cost for biological treatment (pence/cubic metre)
- Ot = COD of trade effluent (mg/l); Os = COD settled sewage (mg/l)
- S = Unit cost for sludge disposal (pence/cubic metre)
- St = Solids value trade effluent (mg/l); Ss = Solids value* settled sewage (mg/l)

Leather Manufacture: Where does COD come from?

- **Beamhouse**
  - A significant amount of the COD contribution comes from the raw material
  - Improvements are usually based on processing and commodity chemical amendments
    - e.g., Hair save
- **Dyehouse**
  - Chemical companies, products and processing parameters play a significant role

Leather Manufacture: Where does COD come from?

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- Proteins
  - Blood, collagen, keratin, interfibrillary proteins
- Fats and oils
  - Natural fats, fatliquors etc
- Tanning and retanning agents
  - Vegetable tannins
  - Glutaraldehyde
  - Syntans
  - Acrylics
  - Polymers
  - Resins
- Acids and alkalis
  - Formic acid, sodium formate, etc

Organic matter

- Compounds that contain carbon
  - Excludes simple oxides, carbonates, cyanides and carbides

Understanding the COD of Proprietary Products

- **The COD contribution of a Proprietary Product is determined by:**
  a) The inherent COD contribution of the individual organic components
  b) The extent to which the organic components are oxidised
  c) The active matter of the Proprietary Product (concentration)

- **Active Matter for the purpose of this study:**
  - Liquid products: Non-water component (water determined by Karl Fischer titration)
  - Powder products: Dry matter determined by heating and gravimetric analysis

Understanding the COD of Proprietary Products

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- **Inherent COD contribution of the individual organic materials**
  - COD can be calculated theoretically (COD_t) according to the balanced equation:

$$C_xH_yO_z + \tfrac{1}{4}\cdot(4x+y-2z)\cdot O_2 \rightarrow x\cdot CO_2 + \tfrac{1}{2}\cdot y\cdot H_2O$$

$$COD_t = \frac{8\cdot(4x+y-2z)}{(12x+y+16z)} \quad gCOD.g\text{-}1\, C_xH_yO_z$$

  - Assuming that the oxidation goes to completion this equation can be used quite effectively to calculate the COD of simple organic molecules composed of carbon, hydrogen and oxygen molecules only

Understanding the COD of Proprietary Products

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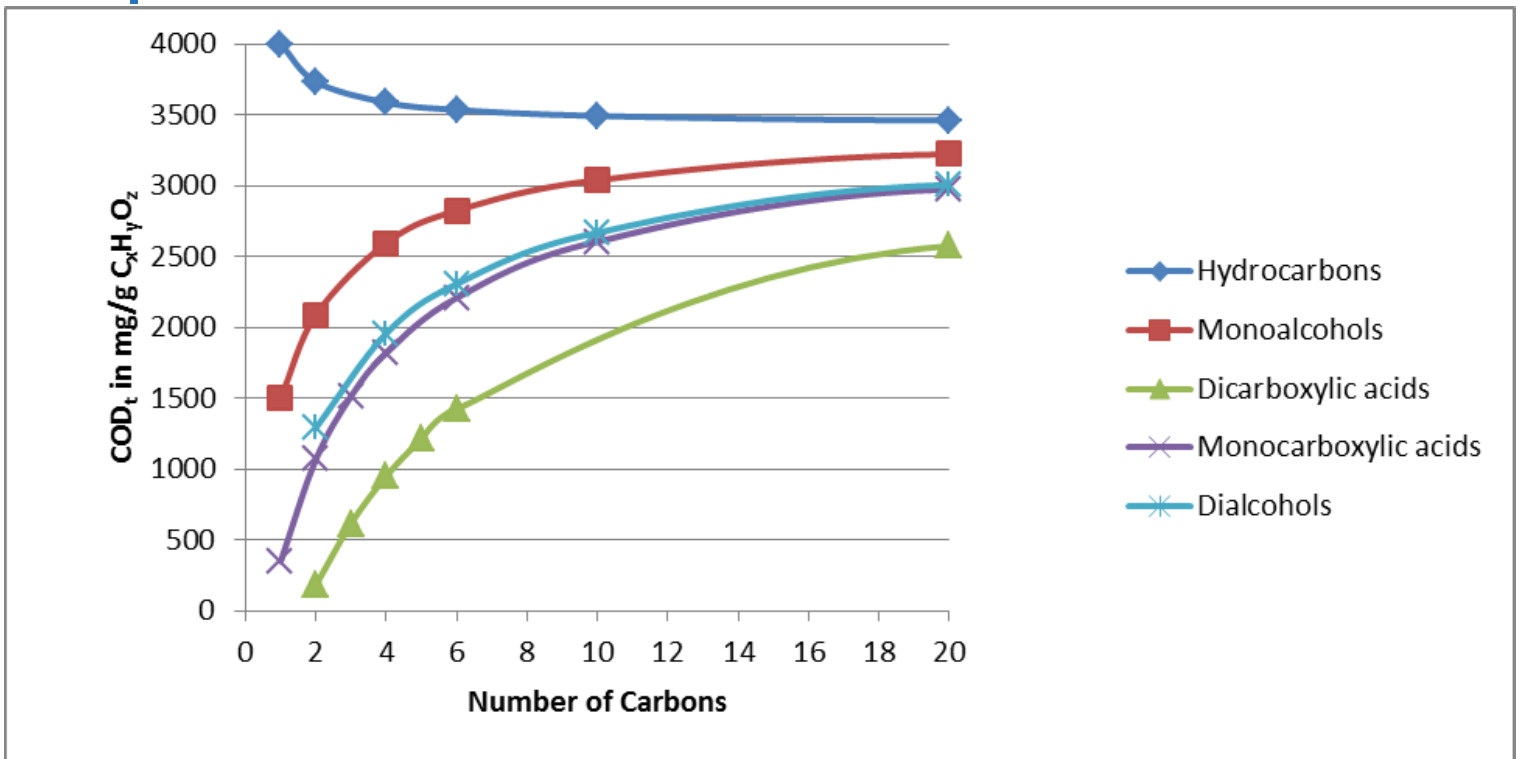
a) The inherent COD contribution of individual organic components



A graph representing theoretically calculated COD values (COD_t) for a range of simple organic molecules with chains up to 20 carbons long.

Understanding the COD of Proprietary Products

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b) The extent to which organic molecules are oxidised during COD analysis

- Most organic compounds oxidise 95-100% c.f. theoretical values
- Some organic molecules may resist oxidation or are lost
  - » e.g., pyridine and volatiles, respectively

Understanding the COD of Proprietary Products

c) The Active Matter of a Proprietary Product

- A Proprietary Product with a high Active Matter will always have a higher COD than a similar product with low Active Matter
- A Proprietary Product with a low Active Matter is not better than a similar product with high Active Matter
  - Dilution of chemicals
- Why would a Proprietary Product have a low COD?
  - The product may not organic in nature (contains non-oxidisable inorganic chemicals)
  - The organic component present has a low inherent COD
  - The product has a low Active Matter

Understanding COD: Fatliquors

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c) The Active Matter of a Proprietary Product

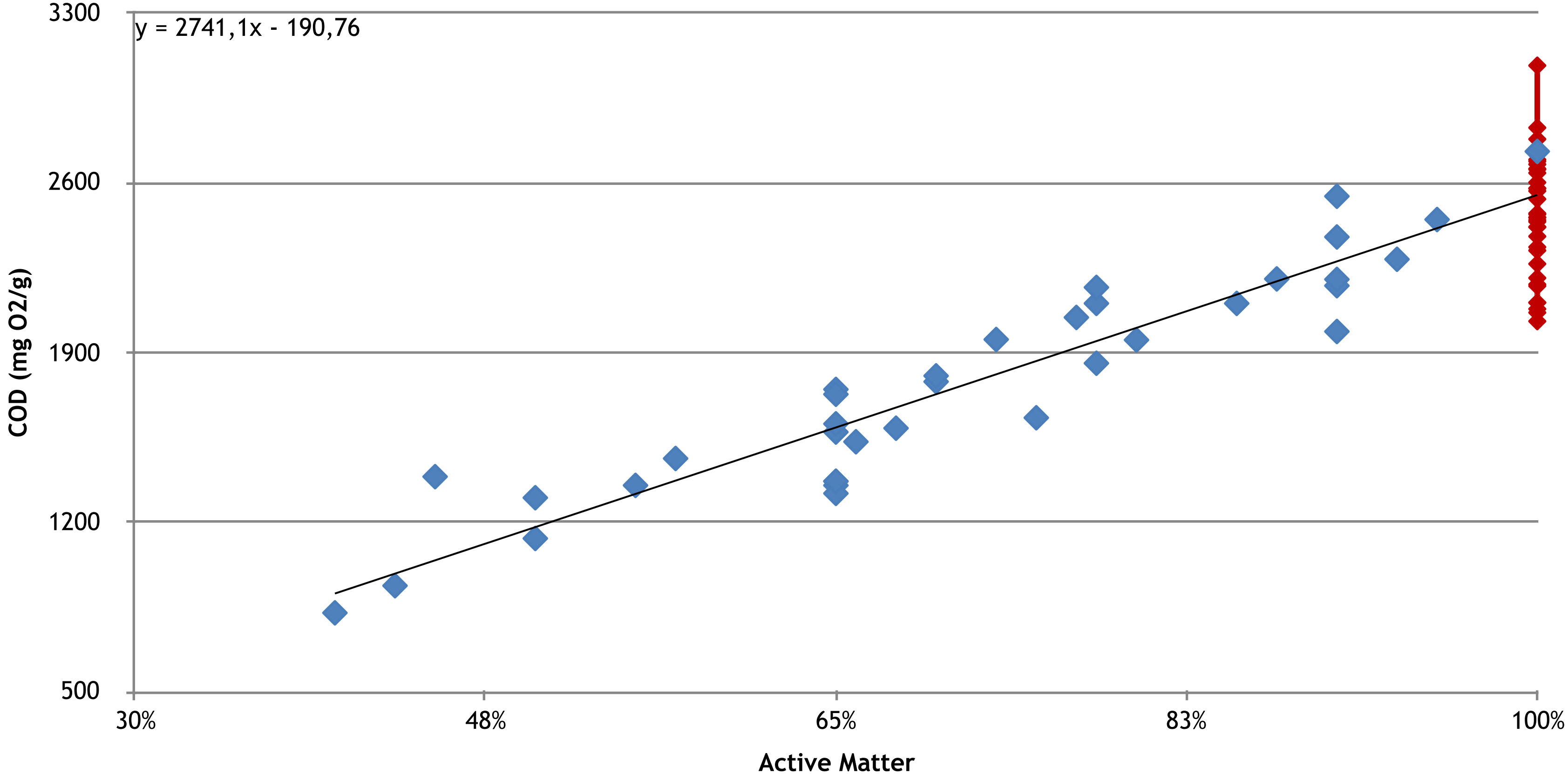

Figure: Measured COD (mg O_2/g) for TRUMPLER Fatliquors plotted versus Active Matter

Understanding COD: Acrylics and Polymers

c) The Active Matter of a Proprietary Product

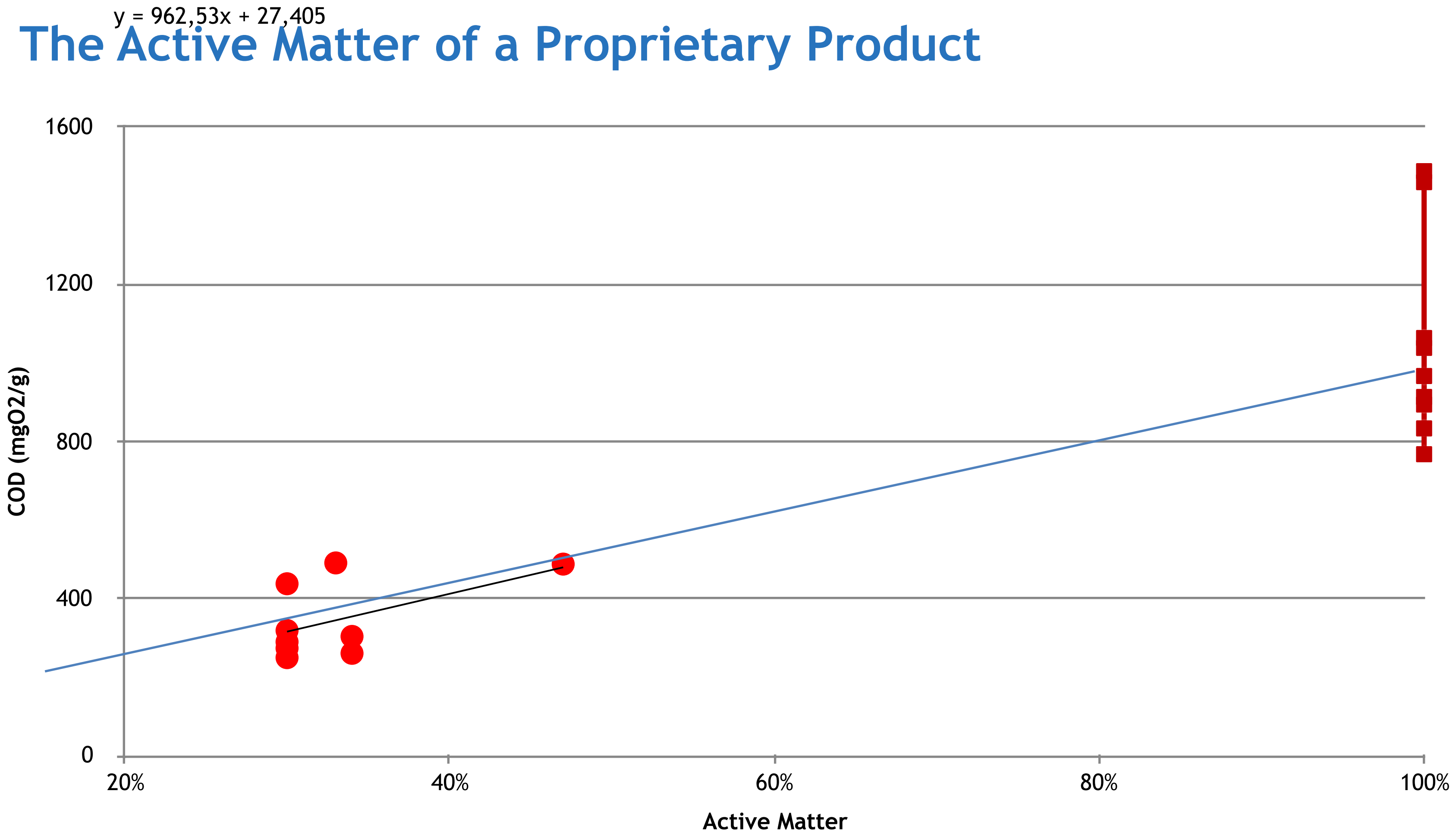

Figure: Measured COD (mg O_2/g) for TRUMPLER Acrylics and Polymers plotted versus Active Matter

Understanding COD: Syntans and Vegetable Tannins

c) The Active Matter of a Proprietary Product

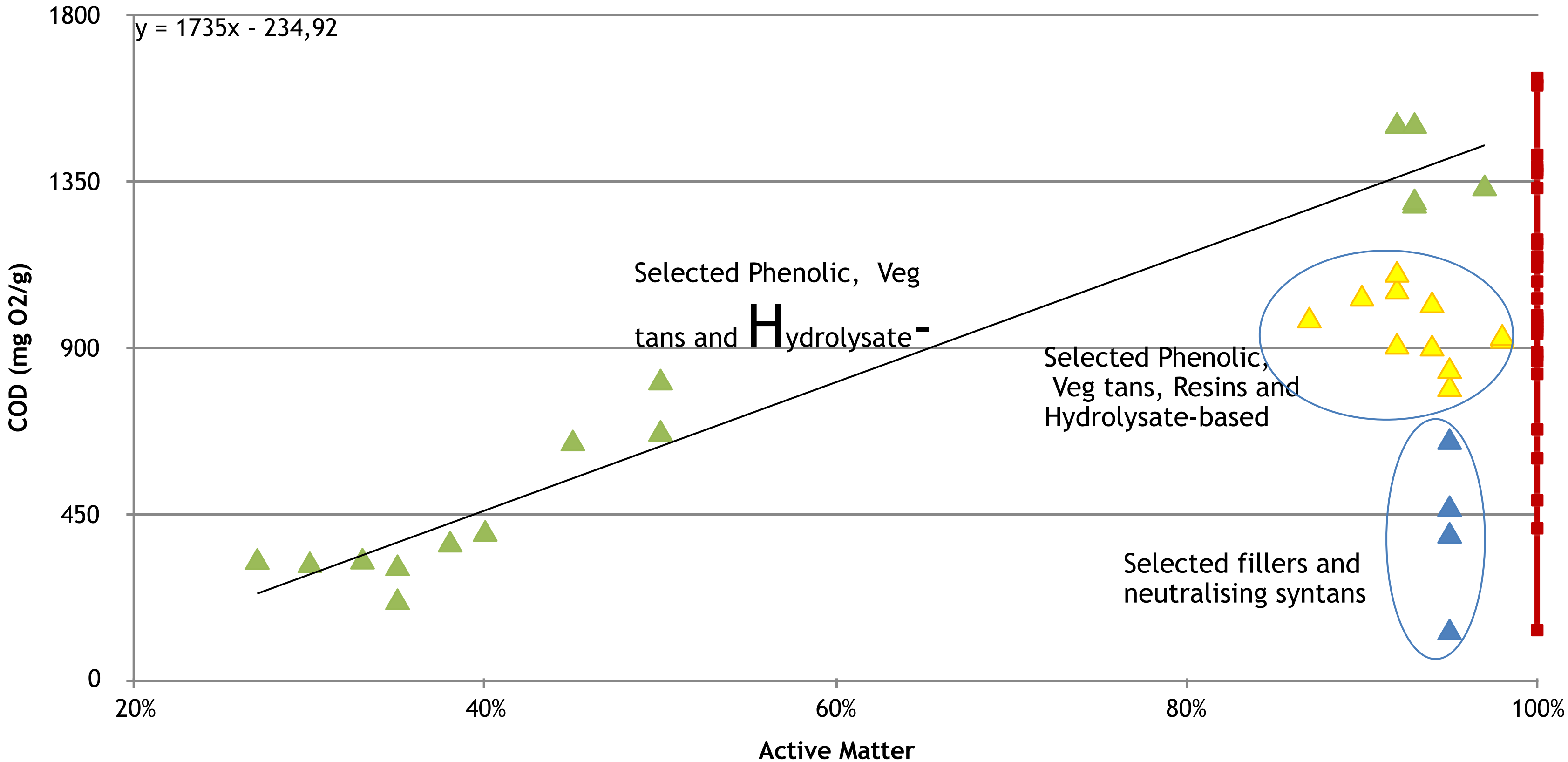

Figure: Measured COD (mg O_2/g) for TRUMPLER Syntans and Vegetable Tannins plotted versus Active Matter

Project Objectives: COD Fatliquors & Retanning Agents

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Is TRUMPLER able to:

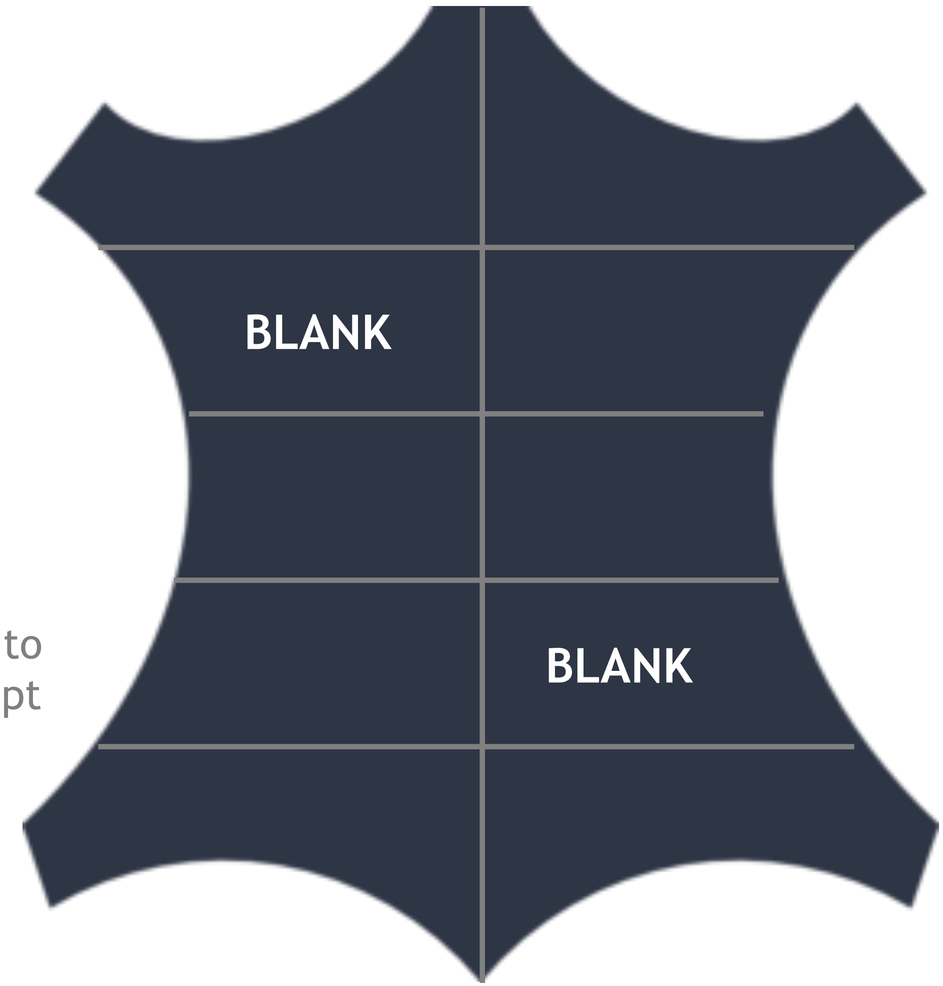
1. Determine which individual products/product ranges are likely to perform well wrt low effluent COD contribution?
   - Can we use the results to express the degree of exhaustion for individual products?
2. Can we use COD results of individual Proprietary Products to predict the COD of effluents in dyehouse recipes?
   - Can we use a mass balance approach for effluent COD

1. Product Exhaustion (COD) Experimental Design

- Wet blue
- "Standard processes" developed for each product range investigated
  - Fatliquors (35)
  - Syntans & Vegetable Tannins (30)
  - Acrylics and Polymers (9)
- A number of parameters were investigated in order to establish the best combinations to ensure:
  - Valid results: enough differentiation between results
  - As close to industrial application as possible
- Synergistic and antagonistic product interactions are possible
  - Attempts were made to minimise these as much as possible in order to establish an individual product assessment

1. Product Exhaustion (COD) Experimental Design

- Wet blue used from the same supplier and the same batch where possible
- Hides were cut into 10-12 pieces
- For every hide, 2 BLANK samples were processed as internal controls
  - A Blank sample is where all processes and times are adhered to and all chemicals are added except the chemical under investigation
  - This allows us to isolate and establish the effect of individual chemicals



1. Product Exhaustion (COD) Fatliquors: Experimental

- **35 Fatliquors investigated**
  - 7%* Fatliquor
    - Based on Active Matter (Water Content – Karl Fischer)
  - Hides and samples prepared using standard procedure
  - Proprietary Product COD Remaining = Float COD – BLANK COD_{Hide}

1. Product Exhaustion (COD) Fatliquors: Experimental

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Process	%	Product	Temp.	Time	Comments
Samples processed together					
Neutralise	300	Water	35		
	2	Sodium Formate		20‘	
	0.3	Sodium Bicarbonate		40‘	pH 5.2-5.5 (Ø Blue BCG)
Retan	3	ACRYLIC		30‘	
	6	PHENOLIC SYNTAN (40%)		60‘	Drain
Wash	300	Water	60	15‘	
Samples separated and processed further individually					
Fatliquoring	200	Water	60		
	7*	FATLIQUOR		60‘	(BLANK)
Fixing	1	Formic acid (1:10)	20	40‘	pH 3.4-3.8
Float sample removed for COD analysis					
Wash	300	Water	20	15	* = Active Matter

1. Product Exhaustion (COD) Fatliquors: Results

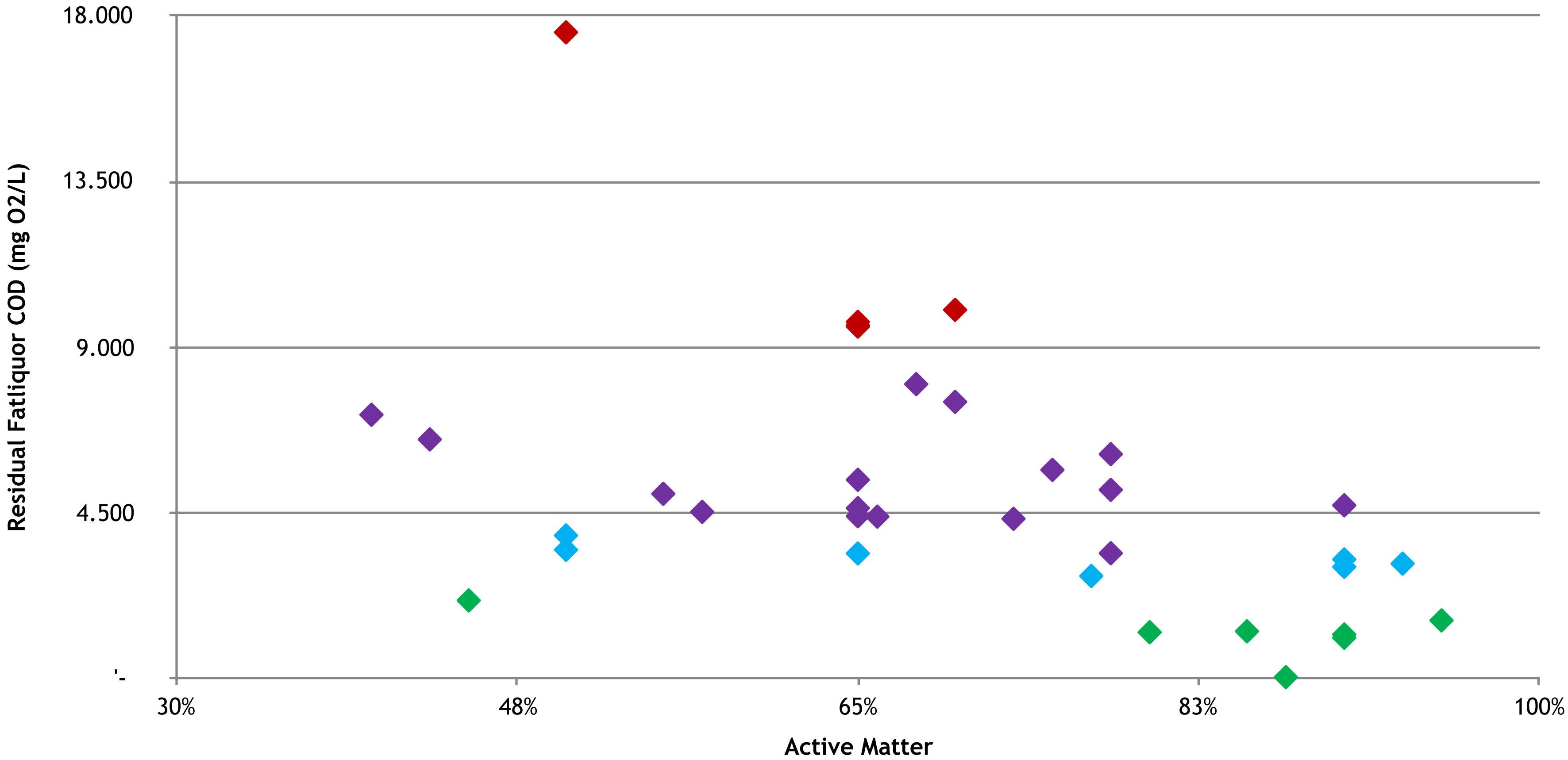

Figure: COD attributed to residuals of proprietary fatliquors plotted versus Active Matter

1. Product Exhaustion (COD) Fatliquors: Results

- **% Exhaustion (COD)**

$$\% \text{ Exhaustion} = 100 - \left(\frac{\text{Residual Product COD}_{meas}}{\text{Product COD Added}_{calc}} \right) x100$$

- How does a graph of "% Exhaustion vs Active Matter" compare to a graph of "Float COD vs Active Matter"?

1. Product Exhaustion (COD) Fatliquors: Results

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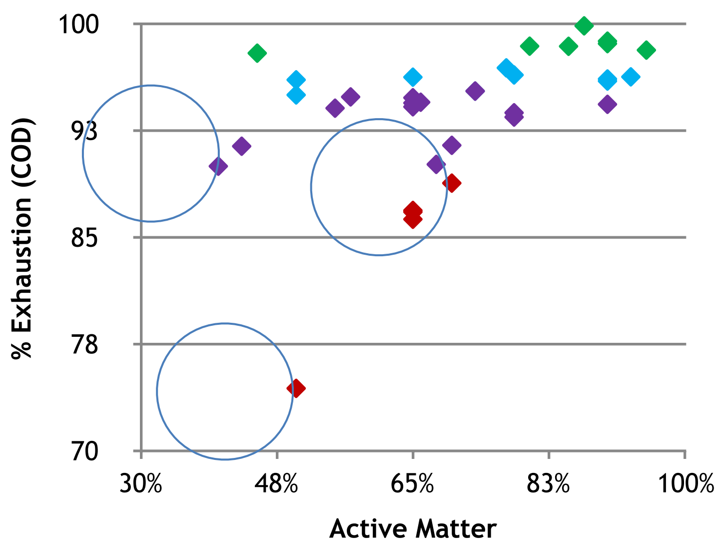
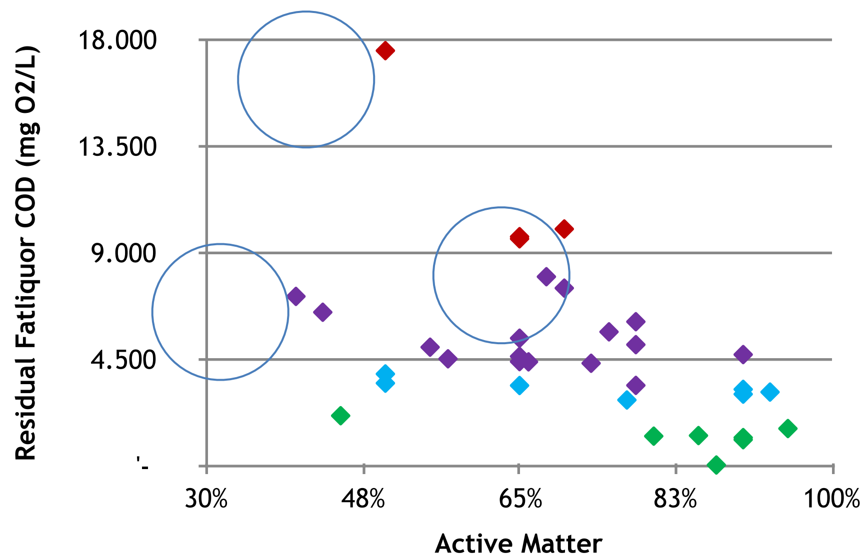
- **% Exhaustion vs Residual COD**
  - Careful experimental design means that graphs are almost mirror images of one another and "% Exhaustion" is used throughout the remainder of the presentation





1. Product Exhaustion (COD) Fatliquors: Results

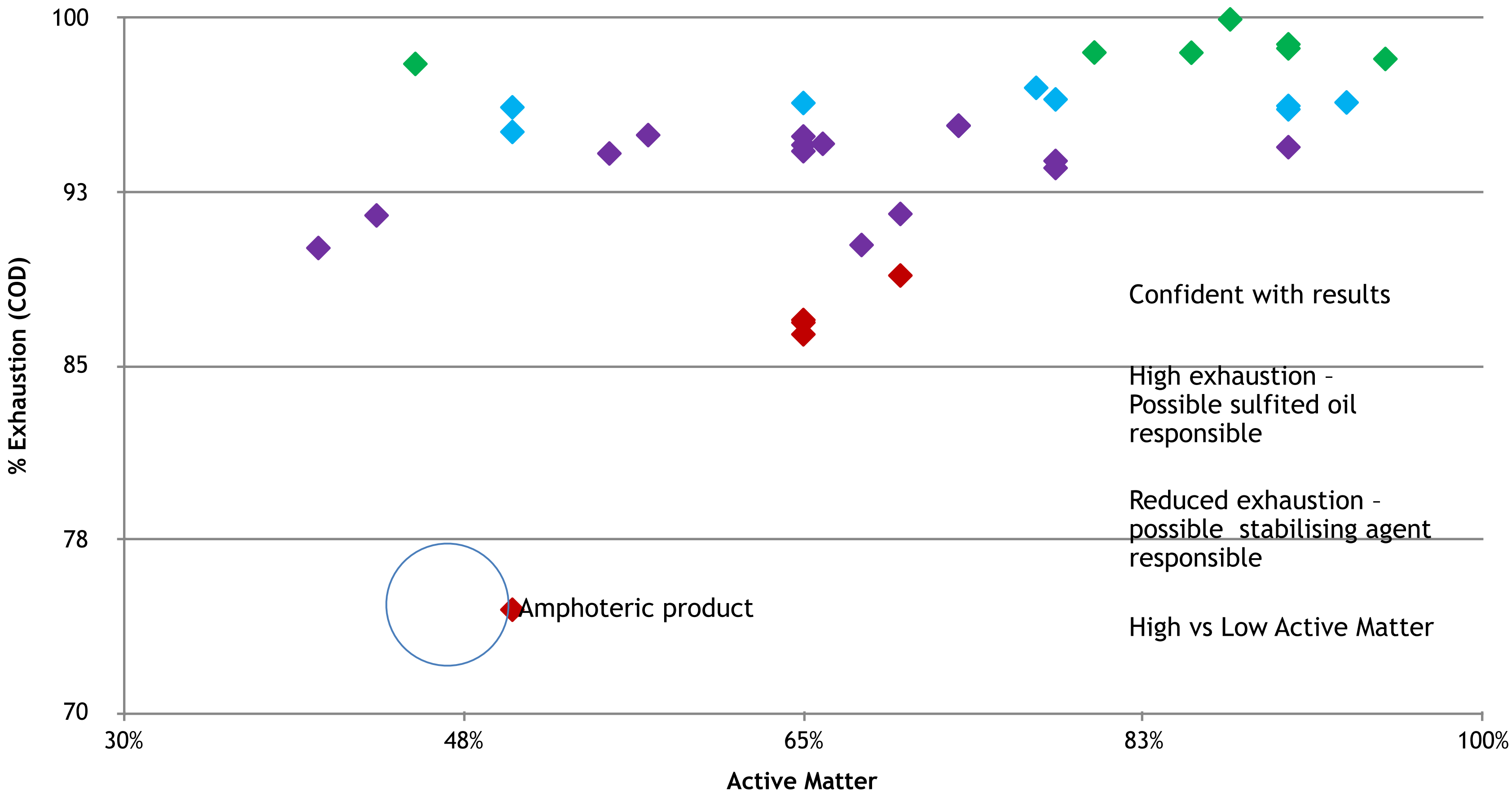


Figure: % Exhaustion of proprietary TRUMPLER fatliquors plotted versus Active Matter

1. Product Exhaustion (COD) Acrylics & Polymers: Experimental

- **9 Acrylics and polymers investigated**
  - 1.8%* Acrylics and Polymers
    - Based on Active Matter (Water Content – Karl Fischer)
  - Hides and samples prepared using standard procedure
  - Chemical COD Remaining = Float COD – BLANK COD_{Hide}
  - % Exhaustion calculated in same way as for Fatliquors

1. Product Exhaustion (COD) Acrylics & Polymers: Results

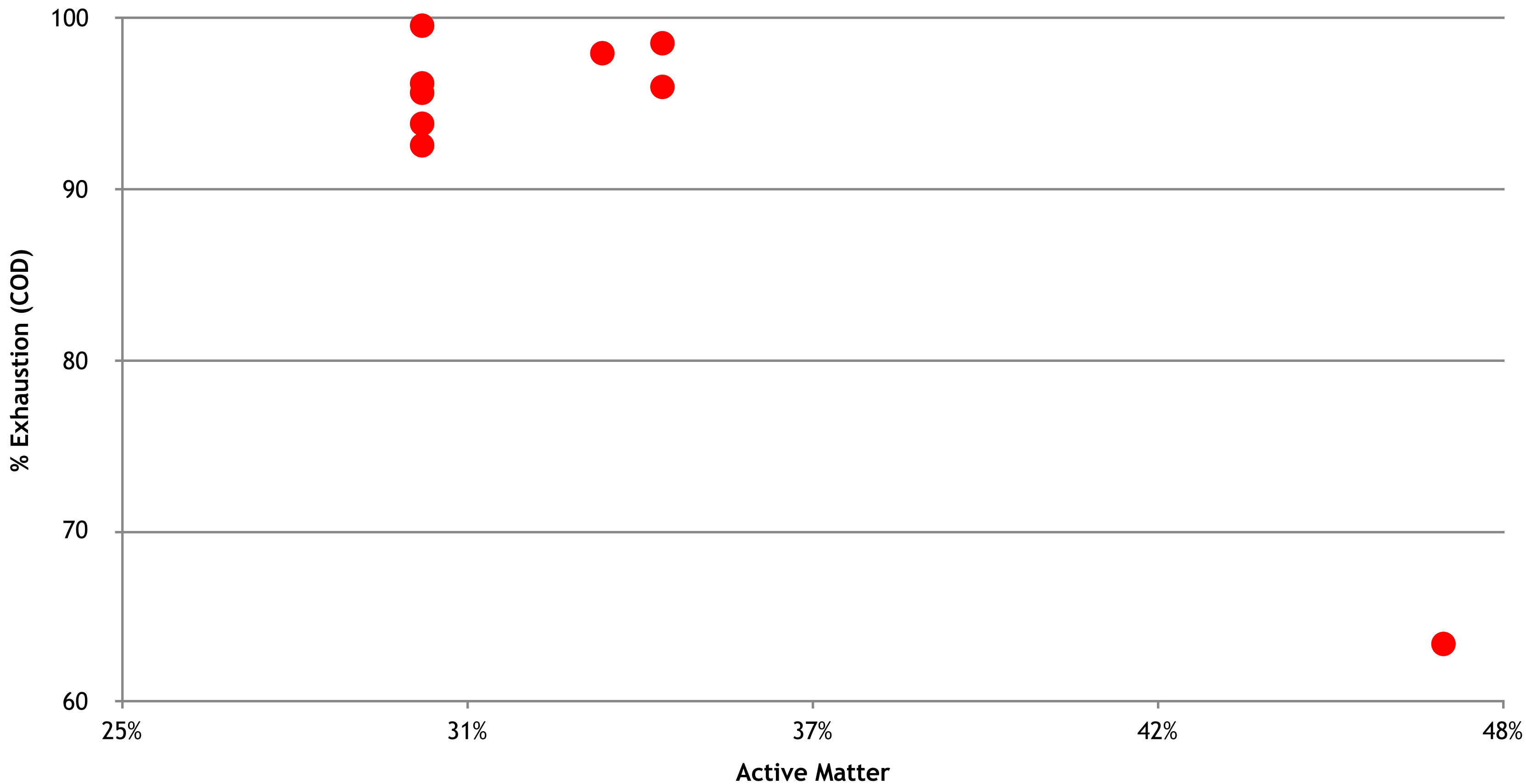


Figure: % Exhaustion of proprietary TRUMPLER Acrylics and Polymers plotted versus Active Matter

1. Product Exhaustion (COD) Syntans & Veg Tannins: Experimental

- **30 Syntans and Vegetable Tannins investigated**
  - 8%* Syntans and Vegetable Tannins
    - Liquids based on Active Matter (Water Content – Karl Fischer titration)
    - Powders based on Active Matter (Dry Matter - Gravimetric)
  - Hides and samples prepared using standard procedure

  - Chemical COD Remaining = Float COD – BLANK COD_{Hide}
  - % Exhaustion calculated in same way as for Fatliquors

1. Product Exhaustion (COD) Syntans & Veg Tannins: Results

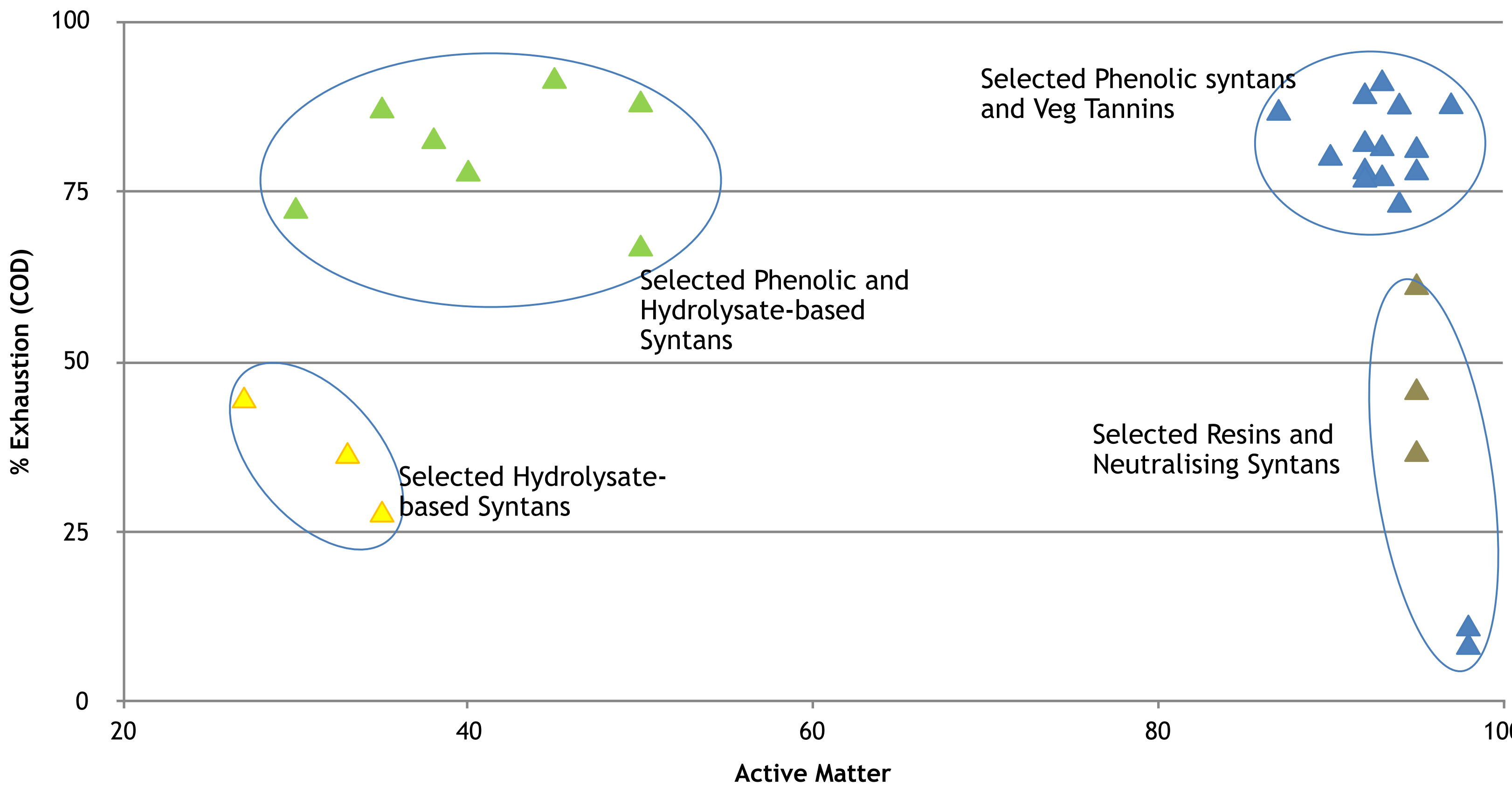


Figure: % Exhaustion of proprietary TRUMPLER Syntans and vegetable tannins plotted versus Active Matter

2. COD Mass Balance Experimental

- **Objective 2:** Can we use COD results of individual Proprietary Products to predict the COD of effluents in dyehouse recipes?
  - Standard Recipes and sample preparation procedures were developed in line with the previous investigation
  - Fatliquors
    - The measured COD contributions of combinations of 3 selected high exhaustion (COD) fatliquors and 3 selected reduced exhaustion (COD) fatliquors were **compared to theoretically calculated COD values of the complete retanning and fatliquoring process**
  - Retanning Agents
    - The measured COD contributions of combinations of 3 selected high exhaustion (COD) “syntans, acrylics and polymers and vegetable tannins” and 3 selected reduced exhaustion (COD) “syntans, acrylics and polymers and vegetable tannins” were **compared to theoretically calculated COD values of the complete retanning and fatliquoring process**

2. COD Mass Balance: Results High Exhaustion (COD) Fatliquors

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Process	%	Product	T	t	Dil.	COD (mg/g)
	100	Water	20			
Retanning	5	ACRYLIC (30%, 96.0%)		20'	1:3	290
	2*	SYNTAN (35%, 87%)		20'		210
	3*	SYNTAN (95%, 78%)		20'		644
	3*	SYNTAN (94%, 87%)		60'		1014
	100	Water	60			
Fatliquor	2.5*	FATLIQUOR A (90%, 98.9%)				2545
	2.5*	FATLIQUOR B (95%, 98.2%)				2449
	2.5*	FATLIQUOR C (85%, 98.5%)		60'	1:4	1952
	2x1	Formic acid (70%, 5%)		40'	1:10	288
Sample collected for analysis						

Predicted COD 7 546mg/L

COD Measured 5 770mg/L

* = Active Matter
(Active Matter, % Exhaustion)

2. COD Mass Balance: Results Reduced Exhaustion (COD) Fatliquors

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Process	%	Product	T	t	Dil.	COD (mg/g)
	100	Water	20			
Retanning	5	ACRYLIC (30%, 96.0%)		20‘	1:3	290
	2*	SYNTAN (35%, 87%)		20‘		210
	3*	SYNTAN (95%, 78%)		20‘		644
	3*	SYNTAN (94%, 87%)		60‘		1014
	100	Water	60			
Fatliquor	2.5*	FATLIQUOR a (70%, 88.9%)				1804
	2.5*	FATLIQUOR b (65%, 87.0%)				1369
	2.5*	FATLIQUOR c (65%, 86.3%)		60‘	1:4	1318
	2x1	Formic acid (70%, 5%)		40‘	1:10	288
Sample collected for analysis						

Predicted COD 14 053mg/L

COD Measured 13 580mg/L

*** = Active Matter**
(Active Matter, % Exhaustion)

2. COD Mass Balance: Results High Exhaustion (COD) Retan

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Process	%	Product	T	t	Dil.	COD (mg/g)
	100	Water	20			
Retanning	5	ACRYLIC (30%, 96.0%)		20‘	1:3	290
	2*	SYNTAN A (35%, 87%)		20‘		210
	3*	SYNTAN B (95%, 78%)		20‘		644
	3*	SYNTAN C (94%, 87%)		60‘		1014
	100	Water	60			
Fatliquor	7.5*	FATLIQUOR (95%, 98.2%)		60		2449
	2x1	Formic acid (70%, 5%)		40‘	1:10	288
Sample collected for analysis						

Predicted COD 7 878mg/L

COD Measured 6 595mg/L

* = Active Matter
(Active Matter, % Exhaustion)

2. COD Mass Balance: Results
Reduced Exhaustion (COD) Retan

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Process	%	Product	T	t	Dil.	COD (mg/g)
	100	Water	20			
Retanning	5	ACRYLIC (30%, 96.0%)		20‘	1:3	290
	2*	SYNTAN a (27%, 44%)		20‘		319
	3*	SYNTAN b (98%, 8%)		20‘		918
	3*	SYNTAN c (92%, 77%)		60‘		1097
	100	Water	60			
Fatliquor	7.5*	FATLIQUOR (95%, 98.2%)		60		2449
	2x1	Formic acid (70%, 5%)		40‘	1:10	288
Sample collected for analysis						

Predicted COD 22 648mg/L

COD Measured 26 451mg/L

* = Active Matter
(Active Matter, % Exhaustion)

2. COD Mass Balance Summary

- **Fatliquor**
  - High Exhaustion (COD) — **COD 23.5% lower than predicted**
  - Reduced Exhaustion (COD) — **COD 3.4% lower than predicted**
- **Syntan**
  - High Exhaustion (COD) — **COD 16.3% lower than predicted**
  - Reduced Exhaustion (COD) — **COD 16.8% higher than predicted**
- **Results are promising and much more accurate than expected but there is some way to go to understand/ predict synergistic and antagonistic interactions**

Conclusions

- **TRUMPLER proposes the following average inherent and oxidisable content COD values for the following dyehouse product groups**
  - Fatliquors (2500mg/g @ 100% AM)
  - Acrylics and Polymeric Retanning Agents (1000mg/g @ 100% AM)
  - Selected Syntans and Vegetable Tannins (1500mg/g @ 100% AM)
- **TRUMPLER can report reliable % Exhaustion and COD results for a significant number of the TRUMPLER Product Range as individual products based on “standard recipes”**
  - Many of the poor performers can be improved significantly by optimisation and the results presented here should not be viewed as final or definitive but merely as a guideline or reference point
- **The COD mass balance provided reasonable correlation between theoretically calculated and practically measured COD values but more investigation is needed in thís area wrt possible synergistic and antagonistic interactions**
- **The % Exhaustion (COD) Product data has already been utilised to identify product ranges and components that may contribute to high and reduced product exhaustion (COD) results**

Future Work

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- **Extend research to wet white raw material**
- **Relate COD data to biodegradability and BOD_5**
- **Include research involving TDS and TKN**
- **Extend research to include the wash floats of selected products to investigate the reversibility of the initial fixation**

- **And Finally,**
  - TRUMPLER will look to build on this research to develop new and improved “COD Friendly” products

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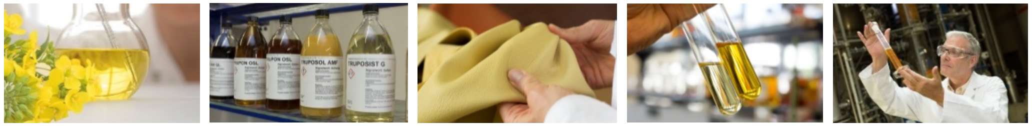
- Innovation & Sustainability
- Partnership & Customized Solutions



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