Alkylphenol Ethoxylate Replacement for Emulsion Polymerization

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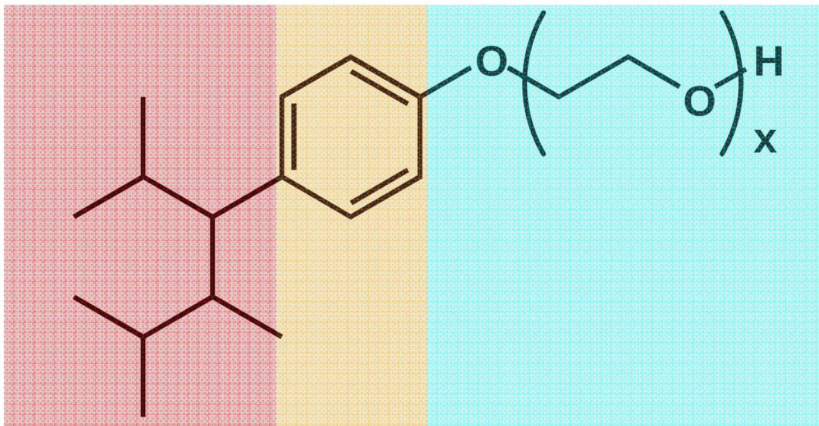
reaching new frontiers

Outline

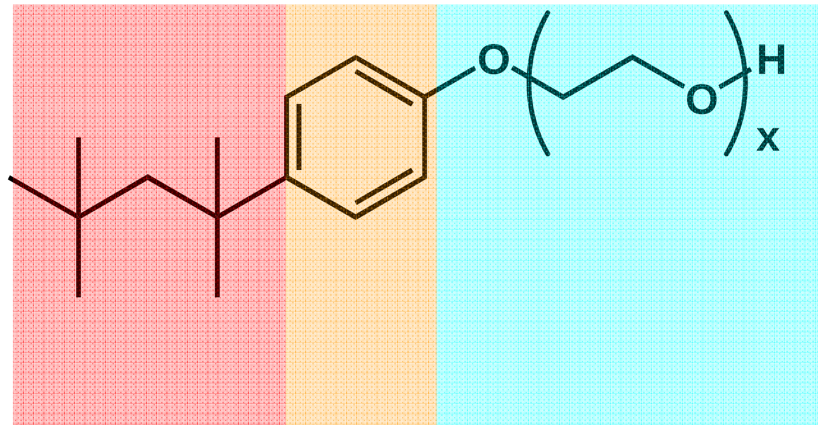
- Introduction
- New Alkylphenol Ethoxylate Alternatives (APEOs)
- Example Emulsion Polymerization
- Analytical Analysis
- Conclusions
- Acknowledgements

Introduction

APEOs' Representative Chemical Structures



Nonylphenol Ethoxylate (NPE)



Octylphenol Ethoxylate (OPE)

APEO Advantages

- Excellent emulsification properties

- Good versatility - useful in a variety of emulsion polymerization types

- Branched structure yields lower solidification points and less gelling than traditional alcohol ethoxylate/ water mixtures

APEO Advantages

- Low levels of free un-ethoxylated phenol; low VOC.
- Narrower range EO adduct distribution compared to base-catalyzed primary alcohol ethoxylates
- Historically APEOs have maintained a lower cost compared to alcohol ethoxylates (AEs)

APEO Disadvantages

- Biodegradation of APEOs is slower than that of other AEs

- As degradation proceeds, the resulting metabolites are more surface active and more toxic than the starting intact APEO structure

- Growing attention on perceived environmental properties of APEOs

APEO Disadvantages

- Increasing petroleum prices
- Limited availability of propylene trimer
- Pressure on historical cost/performance advantages

Current APEO Alternatives

Current APEO Alternatives

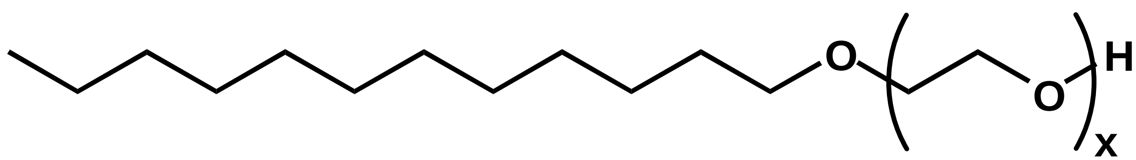
- Linear Alcohol Ethoxylates (LAEs)

- Oxo-Alcohol Ethoxylates

- Secondary Alcohol Ethoxylates

Linear Alcohol Ethoxylates

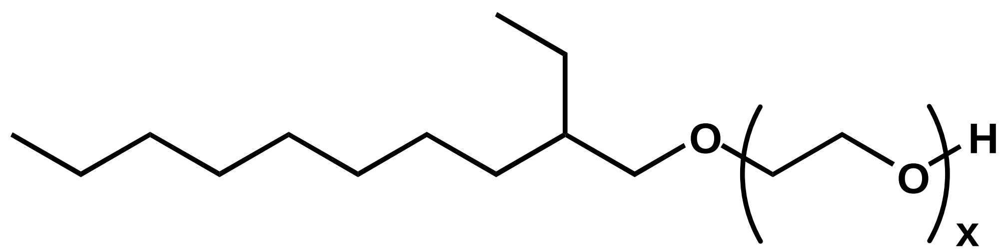
- Advantages
  - Excellent Biodegradation
  - Competitive Costs
- Disadvantages
  - Lack of Branching
  - Increased Pour Points
  - Increased gel phases



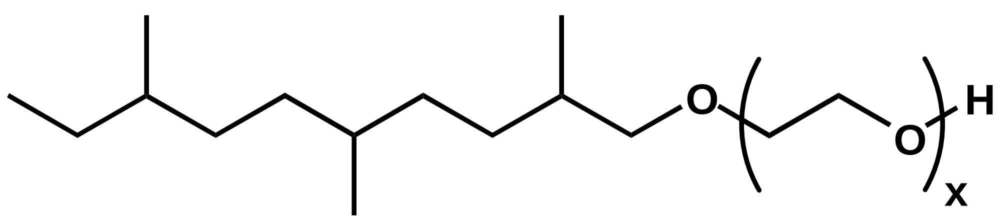
Linear Alcohol Ethoxylate

Oxo Alcohol Ethoxylates

- Advantages
  - Lower Pour Points
  - Fewer Gel Phases
  - Wide Variety of Even/Odd Alcohols
- Disadvantages
  - May be Slower to Derivatize



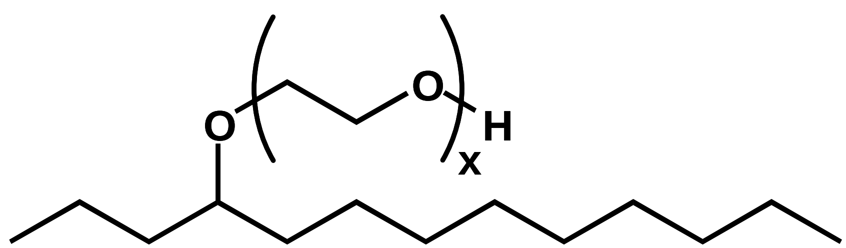
Oxo Alcohol Ethoxylate



Isotridecyl Alcohol Ethoxylate

Secondary Alcohol Ethoxylates

- Advantages
  - Little to No Gel Phases
  - Low Pour Points
- Disadvantages
  - Typically Higher Prices Since More Difficult to Produce



Secondary Alcohol Ethoxylate

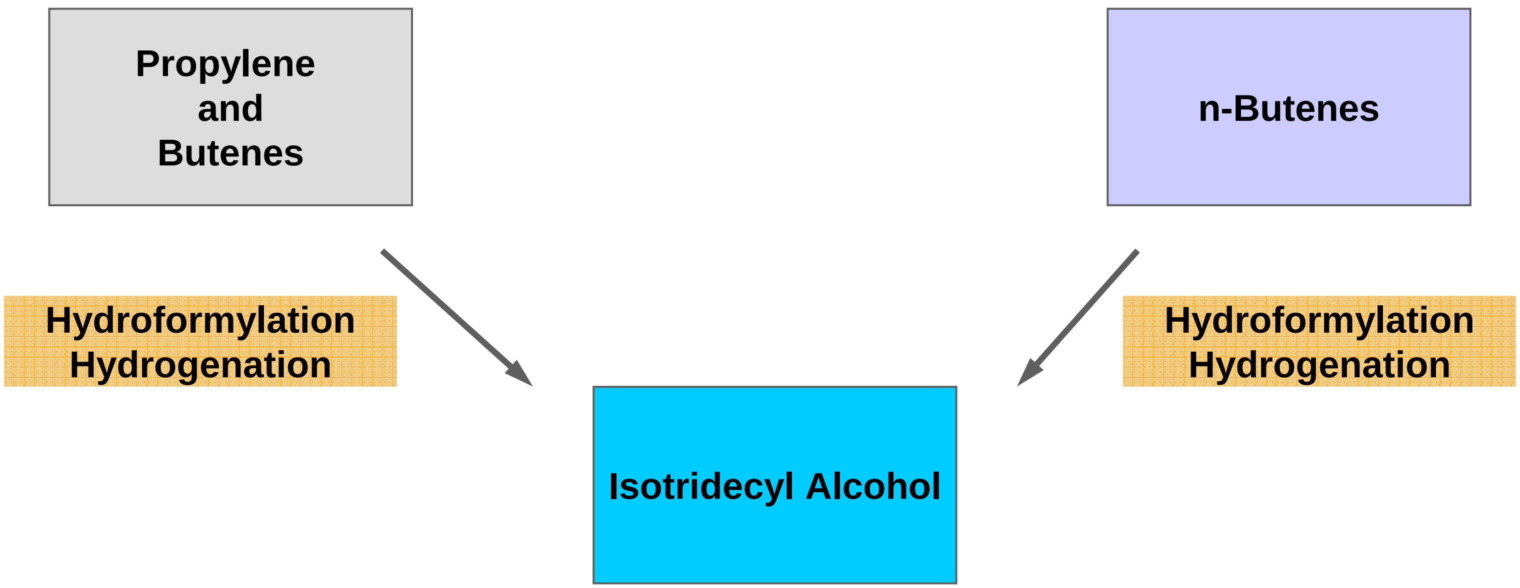
New APEO Alternatives

New APEO Alternatives

- Isotridecyl Alcohol Based on n-Butene
- Fischer-Tropsch (FT) Based Oxo Alcohols
- Use of Narrow Range Ethoxylation Catalyst

Isotridecyl Alcohol Production

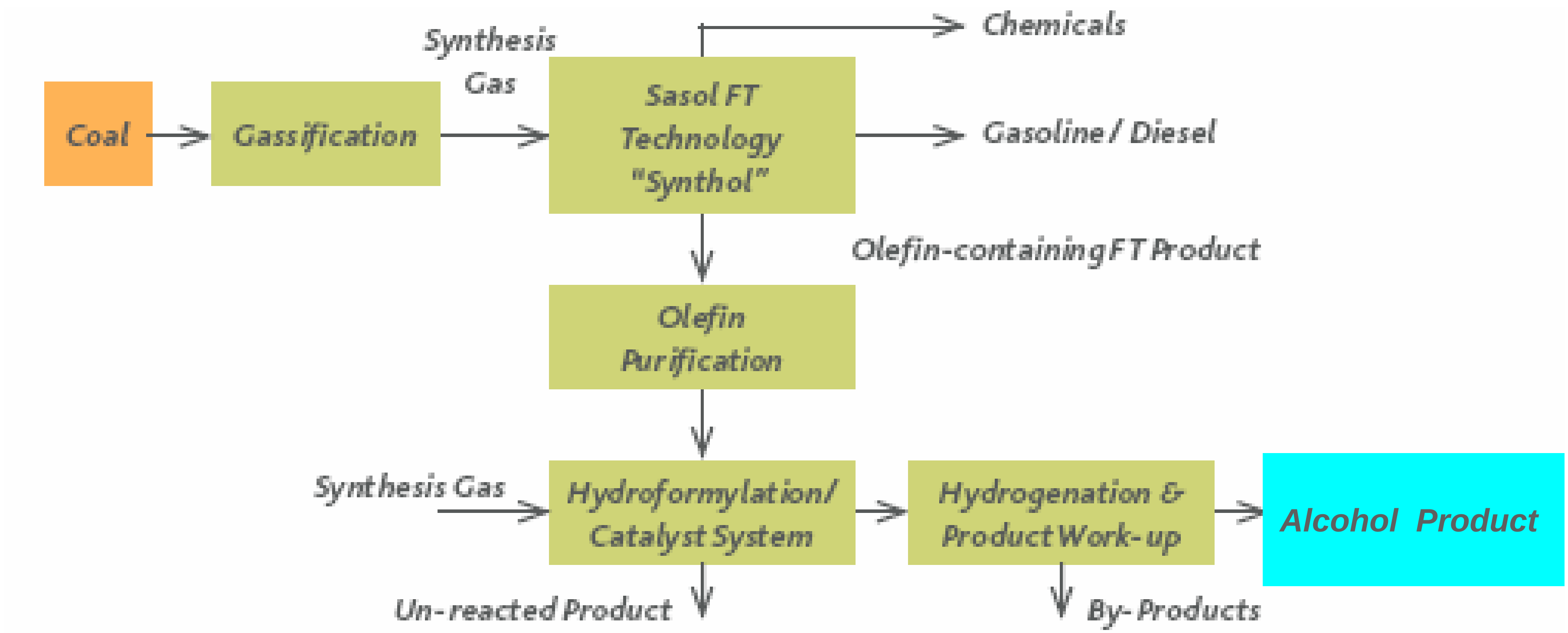
- Oxo Alcohol
- High Degree of Branching
- Compact Hydrophobe



Isotridecyl Alcohols Comparison

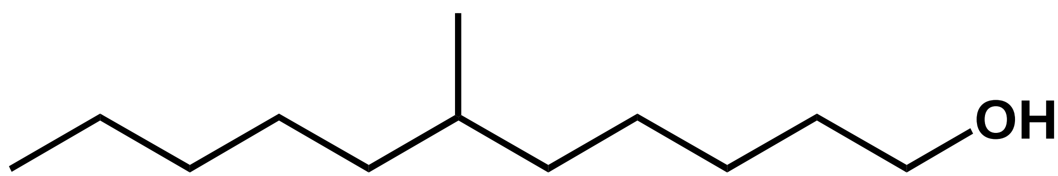
Isotridecyl Alcohol	**Based on C3-C4 Olefin**	**Based on n-Butene**
Carbon Chain Distribution		
C11OH	7%	--
C12OH	30%	--
C13OH	60%	100%
C14OH	3%	--
Average Carbon Chain	12.7	13
Molecular Weight	197	201
Hydroxyl # (mg KOH/gm)	285	279

FT-Oxo Alcohol



FT-Oxo Alcohol

- Linear and Branched Blend
- Unique Branching
- Improved Derivatization (i.e., Ethoxylation)
- Excellent Biodegradation



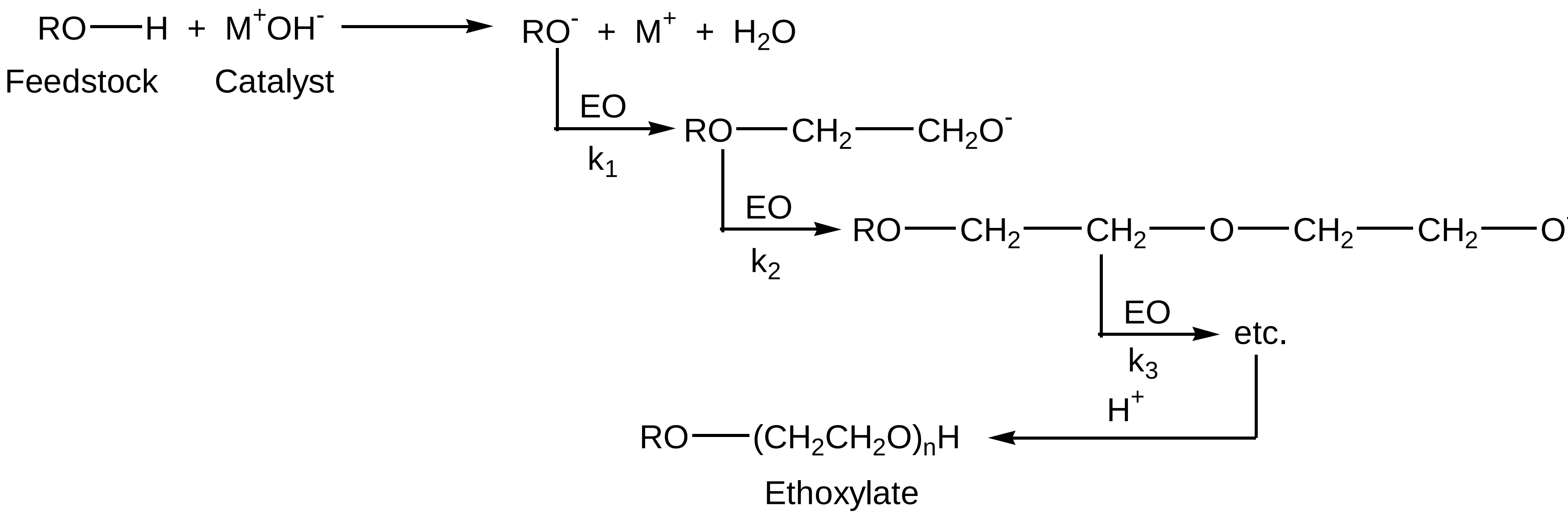
FT-Oxo Alcohol

Oxo Alcohol Comparison

	FT Oxo Alcohol	**Oxo Alcohol**	**Modified Oxo Alcohol**
Olefin Feed	Fischer-Tropsch	Linear	Linear
Hydroformylation Technology	Davy	Un-mod Co	SHOP
Molecular Weight	194	194	194
Carbon Chain Distribution			
$C_{12}OH$	50	42	48
$C_{13}OH$	47	56	51
$HO-CH_2-(CH_2)_n-CH_3$ (linear alcohol)	50%	45%	80%
Total sum of branched alcohols	50%	55%	20%
$HO-CH_2-CHR-R'$ (C2 branched alcohols)	5%	55%	20%
$HO-CH_2-CH_2-R$ (other branching position)	95%	45%	80%
Mono methyl alcohol isomers	30%	14%	8%
Other primary alcohol isomers	20%	<1%	<1%
Quaternary Carbons (Detection Limit 0.3-0.5%)	n.d.	n.d.	n.d.
Total Alcohol	100%	100%	100%

Narrow Range Ethoxylation

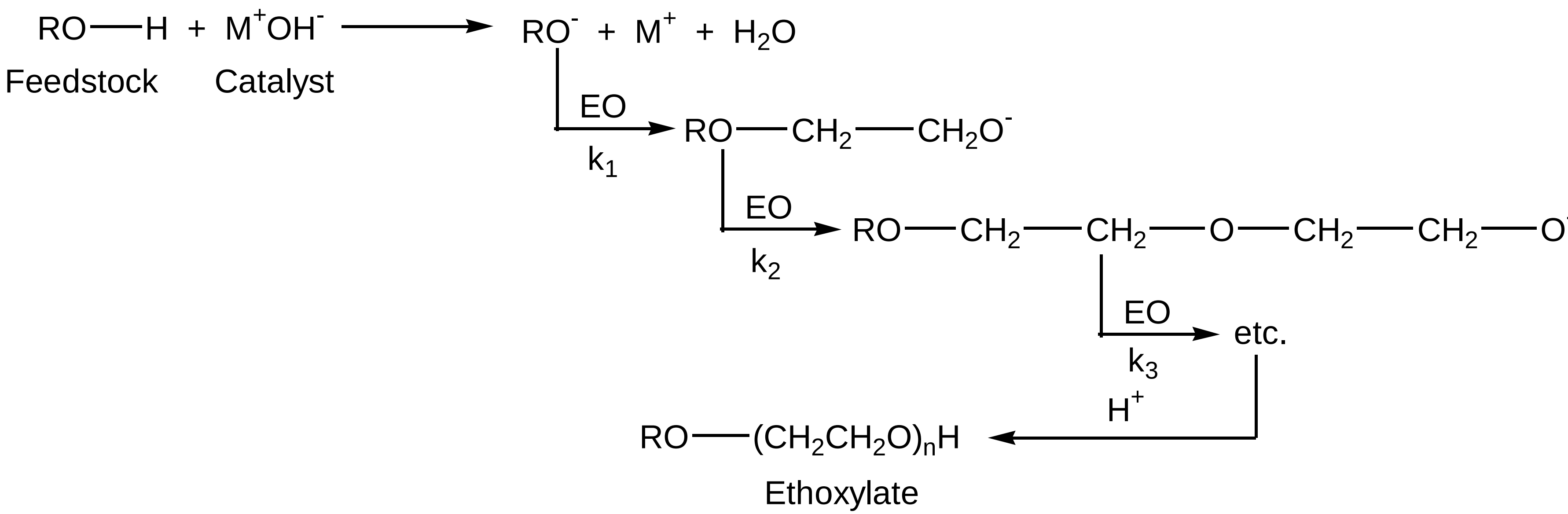
Ethoxylation – Base Catalyzed



$k_1 << k_2 < k_3$

Base catalyzed ethoxylation-
Prefers growing chain to the
starting alcohol

Ethoxylation – Narrow Range Catalyst

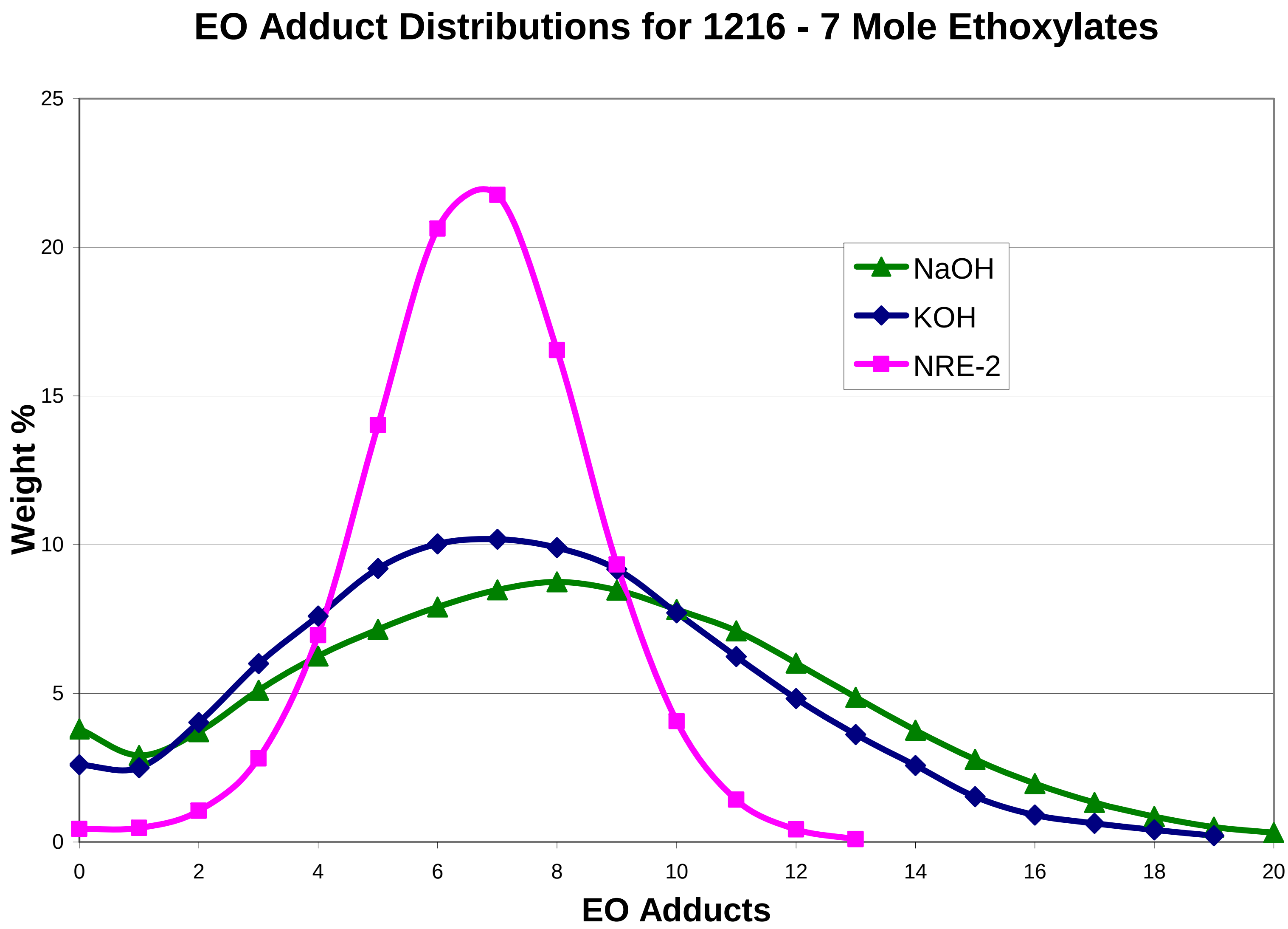


$k_1 < k_2 < k_3$

NR catalyzed ethoxylation- Still prefers growing chain to the starting alcohol but to a **much lesser** degree

LOWER FREE ALOCHOL

EO Adduct Distribution Catalyst Comparison



Comparison of 1216CO-7 Ethoxylate Prepared Using Different Catalysts

Property	**KOH**	**NRE**
Cloud Point (°C at 1% Water)	54	59
Free Alcohol (wt %)	2.39	0.37
PEG content (wt %)	1.47	0.12
Viscosity at °40 (cSt)	27.3	24.8
Melting Point (°C)	3.8	12.8
APHA Color at 60°C	15	8

Narrow Range Ethoxylation - Appearance

0.10% and 0.50% by Weight
of Narrow Range Catalyst

0.10% and 0.50% by Weight
of 45% KOH Catalyst

- Ceteary alcohol 40 mole ethoxylates
- Reaction temperature was 180 ºC
- Picture at ~60ºC

Model Emulsion Polymerization

Styrene-Acrylic Latex Formulation

Ingredient	Grams	Parts bom*
Water	361.14	81.30
Monomer mixture (4 hours feed)		
Butyl acrylate	222.1	50.00
Styrene	211.0	47.50
Acrylic acid	6.7	1.51
Methacrylic acid	4.4	0.99
Aqueous mixture (4 hours feed)		
DOWFAX® 2A1‡ (45%)	5.13	0.52**
Surfactant	2.49	0.56**
Water	88.40	19.90
Sodium hydroxide (20% solution)	2.22	0.10
Initiator solution (4 h 10 min feed)		
Water	88.80	19.99
Potassium persulfate	3.11	0.70
Total	**995.5**	
*** bom – based on monomer** **** based on active species**		

‡from the Dow Chemical Company

Comparative Properties of Nonionic Surfactants Studied

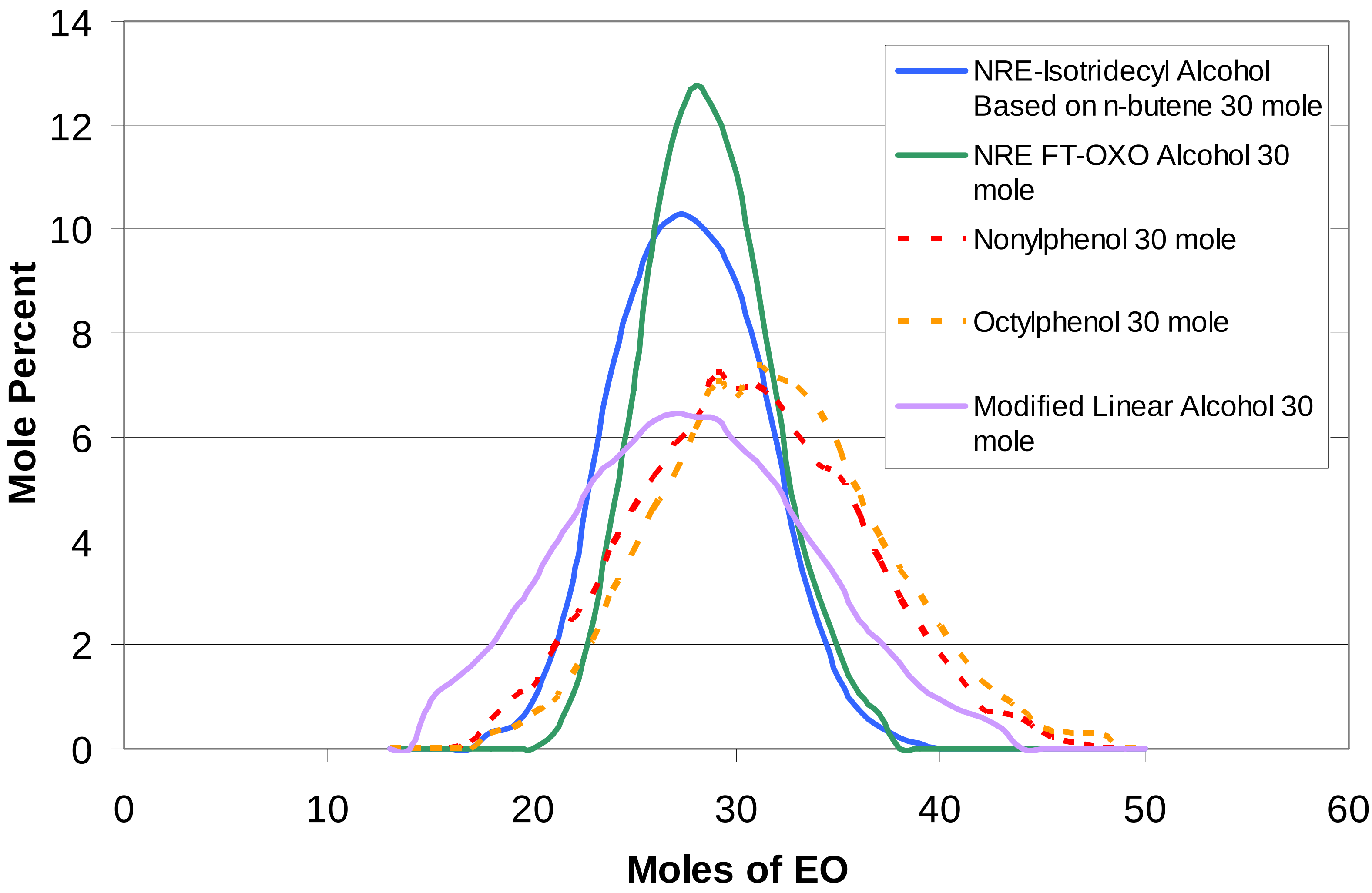
Surfactant	Moles of EO	Active Content %	Cloud point °C	HLB	Appearance
Narrow Range n-Butene-based Isotridecyl Alcohol Ethoxylate	30	100	76	17.3	White Solid
Narrow Range FT-Oxo Alcohol Ethoxylate	30	100	75	17.5	White Solid
Nonylphenol Ethoxylate	30	100	74	17.1	White Solid
Octylphenol Ethoxylate	30	70	72	17.3	Pale Yellow Liquid
Secondary Alcohol Ethoxylate	30	100	74	17.4	White Solid
Modified Linear Alcohol Ethoxylate	30	70	77	17.5	Water-White to Pale Yellow Liquid

Analytical Results

Analysis of the Latex

- MALDI-TOF (Matrix Assisted Laser Desorption Ionization and Time-of-Flight Mass Spectrometry)
- Solids
- Conversion
- Wet Coagulum
- Particle Size
- Minimum Film Forming Temperature (MFFT)

EO Distribution via MALDI-TOF



Latex Properties

Nonionic Surfactant	Solids (%)	Wet Coagulum (%)	Conversion (%)	Particle Size (nm)	MFFT (°C)
Narrow Range Isotridecyl Alcohol Based on n butene Ethoxylate	45.1	0.07	99.2	343	19.8
Narrow Range FT-Oxo Alcohol Ethoxylate	45.2	0.03	99.4	313	22.4
Octylphenol Ethoxylate	45.0	0.07	98.9	385	20.0
Nonyl Phenol Ethoxylate	45.3	0.18	99.6	269	18.8
Secondary Alcohol Ethoxylate	45.1	0.21	99.3	317	17.9
Modified Linear Alcohol Ethoxylate	45.2	0.40	99.3	359	19.6

Conclusions

- APEOs under pressure due to perceived environmental concerns and increasing production costs

- Marketplace seeking cost-effective APEO alternatives

- Current technologies are acceptable, however…

- New narrow range ethoxylates based on new alcohol feed stocks have improved properties making them equal to or more effective than APEOs in emulsion polymerization

Acknowledgements

- Samantha Ingalls

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Thank you for your attention