Challenges and Opportunities with Liquid Ag Product Formulations

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Agenda

I. Formulation Design Considerations

A. Biological

B. Commercial/Market Place

C. Technical

II. Assessing Liquid Re-formulation Options

A. Changing solvents

B. Changing to solid a.i. formulation types

C. Advanced Technology Formulations

III. Industry Progress and Trends

IV. Path Forward

Formulation Design Considerations

Market Place
- Grower Cost
- Use Rates
- Safety
- Liquids Preferred

Technical Parameters
- AI Solubility
- Shelf life

Design Product
- Formulation

Biological Parameters
- Efficacy
- Crop safety

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Biological Parameters

- Minimize the amount of active ingredient (a.i.) applied
  - Lowest field rate (lbs/acre) necessary for crop protection
  - Reduces crop residue and environmental exposure
  - Reduces mixing/loading worker exposures
  - Reduces packaging, shipping, warehousing
  - Minimizes treatment cost for growers

Commercial Considerations/ Market Place Needs

- Grower cost
  - Economical and effective crop protection
    - High impact – Lowest a.i. use rates per acre
- Handling properties
  - Ease of use – Liquids preferred
  - Convenience – Prefer highest possible concentrations
  - Safety – Minimize PPE needs
- Tank mixable with other formulations
- Compatible with existing application equipment

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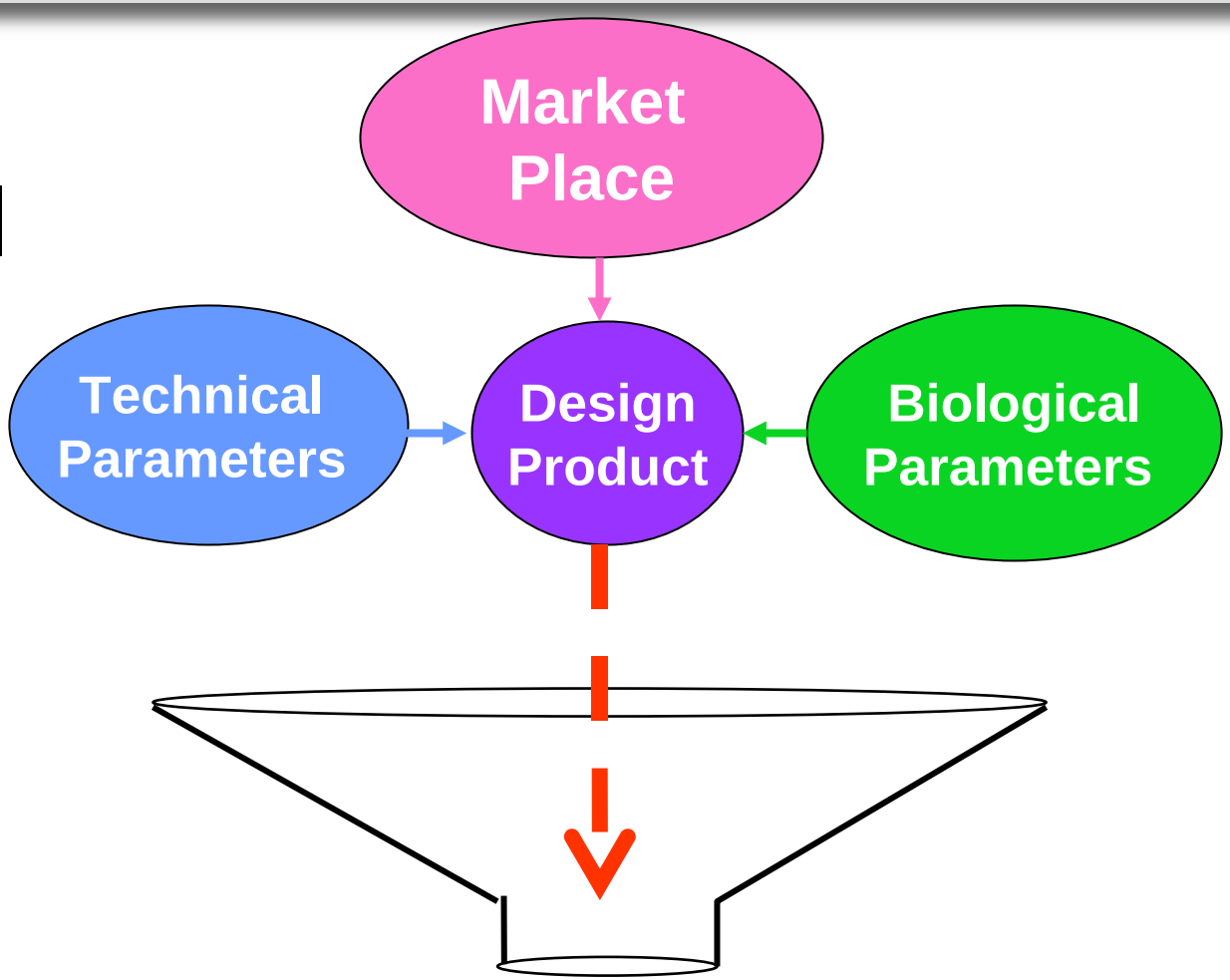
Technical / Formulation Parameters

- Maximize active ingredient concentrations
- Maximize formulation shelf life
- Maintain chemical and physical stability at elevated temperatures representing warehouse storage
- Safe handling properties

Primary Formulation Design Goal



Minimize the use rate of active ingredient per acre

Liquid Product Reformulation Options:

Option A – Change solvents

- EC – Change to lower volatility solvent

Option B – Change to a solid a.i. product

- Solid a.i. forms – WG, WP, SC or other

Option C – Advanced Technologies

- Encapsulation

Criteria for Replacement Solvent Criteria

- Reduced volatility (passes 115ºC TGA test)
- US EPA tolerance exemption for crops
- Non-miscibility with water
- Maintain a high % a.i. concentration formulation
  - Requires saturation solubility < 40ºF for storage and transport
- Chemical compatibility with a.i for long shelf life
- Crop Protection
  - Equivalent efficacy and crop safety

Example Replacement Solvents

- Methylated seed oils
  - Highest solvency (C12) – fails TGA test
  - Passes TGA test (C18) – but poor 40ºF solubility for a.i.
- Seed oil based solvents less stable than petroleum distillates
  - More active needed to maintain efficacy
  - Shorter shelf life results in chemical waste issue
  - Antioxidants required to avoid rancidity
- Cost dilemma
  - Higher solvent costs vs EPA approved petroleum solvents
  - Reduced solvency = Lower concentration product
  - Requires more containers, added transport and warehouse costs

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Example: Solubility Impact on Formulation

Solvent	Solubility at 40°F	Lbs a.i. / gallon	%Wt Solvent In formula	Solvent / Acre (relative)	Example: Cost per 1 Acre Treatment
Xylene	40%	3.0	61%	1X	$3.86
Aromatic 100 + cosolvent	33%	3.0	62%	1X	$4.11
Aromatic 100	29%	2.5	66%	1.3X	$4.36
Aromatic 200	26%	2.0	70%	1.7X	$5.43
C12 – Methylated seed oil	~18%	1.5	75%	~2.4X	$7.05

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Summary: Option A - Change Solvent

- Few solvents meet current TGA test standard
  - TGA fails to consider a VOC's atmospherically availability to form ozone
  - TGA may unnecessarily limit possible solvent options
- Changes to lower vapor pressure solvents may have unintended consequences
  - Lower a.i. solubility results in higher solvent usage
- California growers participate in a competitive global marketplace
  - Expect increased costs for the same crop protection benefits
  - Lower concentrated products - less convenient with more package waste
- Ozone reduction cost:benefit question
  - Do we understand solvent trade-offs in terms of ozone reduction benefits?
  - Based on the SJV inventory data, VOC emissions have been reduced by 2/3rds since 1980, yet ozone levels have not been significantly reduced

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Key A.I. Attributes for Solid Formulations

- Desired a.i. physical/chemical properties
  - High melt point
  - Stable crystal form
  - Safe for particle size reduction (micronization to ~1-10 microns)
  - Safe for WG agglomeration processing
  - Low water solubility (for SC's)
- Reformulation options and needs vary widely based on specific a.i. phys/chem and biological properties
  - Some a.i.'s have better efficacy delivered to the target surface as a liquid solution vs a solid

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Solid A. I. Formulation Options – Melt Point Dependent

- High melt point a.i. (> 100ºC):
  - High concentration SC, WP or WG are possible options
- Moderate melt point a.i. (> 60ºC)
  - Formulation as WP or WG formulations may be possible
  - SC formulations may be susceptible to Ostwald's ripening – crystal growth
- Low melt point (< 60ºC)
  - Particle size growth and caking are common in WP and WG's – unacceptable for use
  - SC formulations often susceptible to crystal growth
- Low/Medium Melt Point a.i. WG and WP Issues
  - Process requirements result in low concentration formulations
  - Reduced shelf stability
  - Customers prefer liquids

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Reformulation - Best Options for Solid A.I. Formulations

- Suspension Concentrates (SC) – Liquid formula contains solid a.i.
  - Micronized particle dispersion in an aqueous continuous phase
  - High customer acceptance – Liquid is easy to measure and pour

- Wettable Powders (WP) – Dry formulation
  - Micronized powder containing surfactant, diluent and a.i.(s)
  - Not preferred by customers – dusty and difficult to measure
  - Lowest cost – Minimal processing required – (Dry blend and micronize)

- Water Dispersible Granules (WG) – Dry formulation
  - A.I., surfactant, diluent and process additives are micronized
  - Powder is agglomerated with moisture, densified and dried with heat

- Dry formulations have lower customer acceptance vs liquids

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Advanced Technology Formulations

- Formulation of low/moderate melt point active ingredients may require advanced technologies:

- Encapsulation
  - Involves significant technology and capital investment
    - Extended product development times vs. conventional products
  - Solvent-free may not not always possible
    - Still may not pass TGA test
    - Increased need for environmental fate modeling assessments
  - Concerns with return on technology investment
    - Will customers de-select new products due to added costs?

Opportunities for Possible EC Reformulation

- Change Solvents
  - Few alternate low VOC solvent options
  - Need realistic estimates of emissions and atmospheric availability
- Convert to solid a.i. formulations
  - Best suited for high melt point a.i.'s
  - Special manufacturing/processing equipment required
  - Dry solid a.i. formulations often de-selected by customers
- Application of advanced technologies
  - Possible option for low/moderate melt point a.i. reformulations
  - Concerned with customer's willingness to pay for increased costs

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Challenges to EC Reformulation

- "Simply reformulate" = "oxymoron"
    - Not simple – impacts entire global product supply chain
    - Technological/Commercial/Biological Constraints
- Time/Cost
    - Significant time/resource investment
    - Best Case ~$0.5 MM
    - Cost escalates for regulatory mandated biology trials
    - Advance technology requires significant investment
- Critical to assure reformulations provide meaningful ozone reduction
- Possible regulatory incentives or credits?

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Industry Progress and Future Trends

Current formulation trend is already moving away from ECs

- Avoid use of highly volatile solvents – i.e. xylene
- Reduced odor, worker exposure, label restrictions
- Improved product handling safety (higher flashpoints)
- Continuing EC displacement by new low use rate a.i. products
- Commercialization of advanced technology formulations
  - i.e. fruit fly bait formulations, termite control technology

Industry Progress - Recently registered products

- Informal survey of WPHA members, only 17% of new products for California from 2002-2004 were EC formulations.

- 83% were non-EC formulations
  - Water-based suspensions
  - Water dispersible granules
  - Wettable powders
  - Baits
  - Etc

Additional Agricultural Progress

- Application Technology Improvements to continue:
  - Improved deposition at target site
  - Improved retention at target site
  - Reduced off-site movement (air & water)
- Best Management Practices to continue:
  - IPM practices continue, scouting, economic thresholds,
  - BMPs for Surface Water benefit Air Quality

Path Forward

- Encourage continued research for root causes of ozone formation (VOC vs. NOx)
  - Support sound science to understand VOC & NOx sources that most impact ozone formation in the San Joaquin Valley
- Value opportunities to work with CA DPR, ARB to improve California air quality
  - Recommendations for State Implementation Plans
  - Balancing multidimensional CA business/environmental needs
- Industry is committed to support a multi-disciplinary working group
  - Industry, suppliers, academia, regulators (local, federal & global) joint efforts to understand and address air quality issues