How pine forests, one of the world's largest biomass, also become a feedstock for the F&F industry.

by Alain Frix, Allchemix Consultancy

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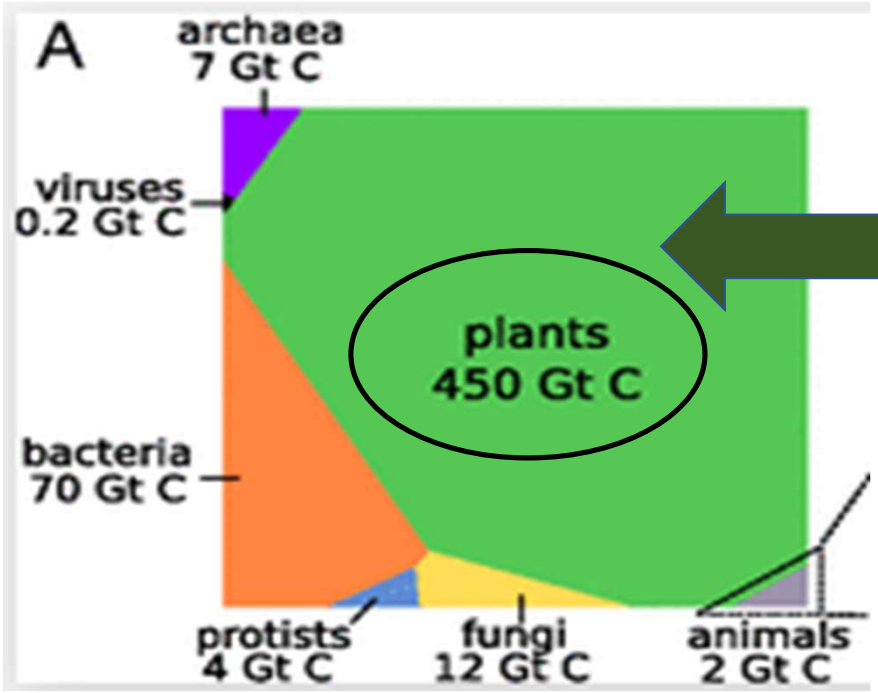
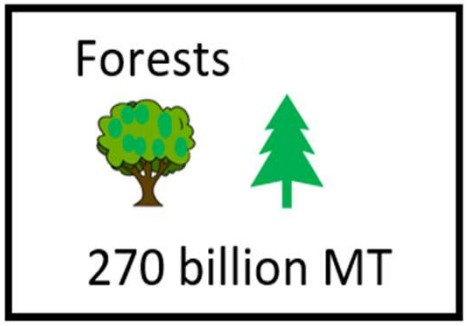
The following slides are part of a presentation given by Alain Frix at PCA Annual Conference in Denver Colorado, USA on September 26th 2022.

Pine Chemicals Association, Grand Hyatt Downtown, Denver, Colorado, USA 25-27 September 2022



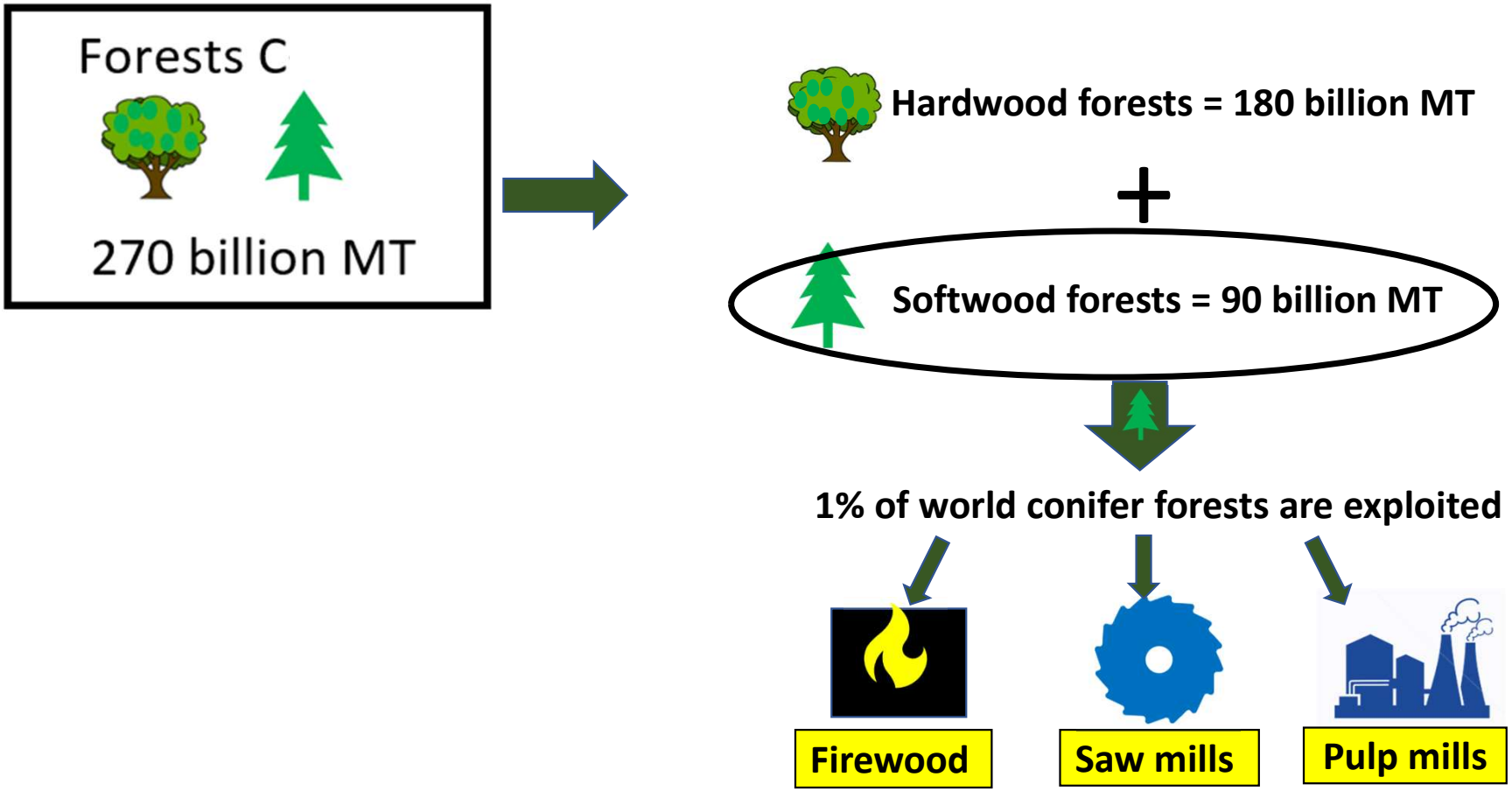
World C Biomass inventory (UN FAO)

World's biggest biomass are plants (450 Gigaton of Carbon = 450 000 000 000 tons of Carbon)
Most of plants are terrestrial.
Trees constitute the biggest plant biomass : 270 Gt C



Hardwood forests = 180 billion MT of C

Softwood forests = 90 billion MT of C

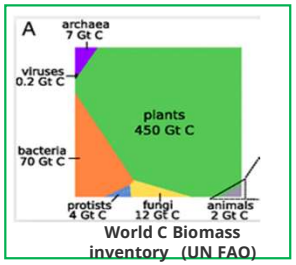


GLOBAL SOFTWOOD BIOMASS FLOW TO MARKETS

Conifers dry biomass, generally :
42% **cellulose** (glucose long polymers) 3 xlonger than hardwoods
27% **hemicellulose** net (crossed polymers various sugars)
28% **lignin** rigidity (polymers of phenylpropane units)
Extractives :

- mainly resin acids, tryglycerides (bark and stem),
- fatty acids, steryl esters, sterols, and lignans (bark and branches)
- Terpenes as VOC's : alpha pinene beta pinene bornyl acetate etc (there are over 40,000 different types of terpenes in nature… lots of functions including protection (insect, heat, etc.)
- Thousands of other chemicals

It is estimated world pine forests naturally release each year 430 millions tons of terpenes (Schenk GO (1979) Möglichkeiten der Ultraviolet-Bestrahlung zur Entkeimung von Brauchwasser. Pafr Kosm 60:397)



World C Biomass inventory (UN FAO)

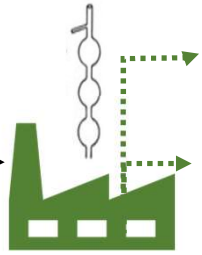
GLOBAL SOFTWOOD BIOMASS FLOW TO MARKETS

TAPPING

collect ~ 880,000 MT oleoresin, avg yield 4 Kg per tree times year

TAPPING

Tapping : access 260,000,000 MT biomass trees alive, only resin collected

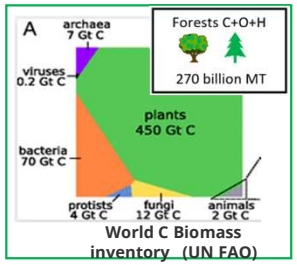


F&F ingredients, Polyterpenic resins, Camphor, Solvents, etc

~17% GT Natural "gum" Turpentine 150 000 mt

~70% Gum Rosins (90% resin acid) 730 000 MT

Pine Resins 1,120,000 mt (Adhesives,inkt,tires, coatings, sealants,sizing…)



World C Biomass inventory (UN FAO)

GLOBAL SOFTWOOD BIOMASS FLOW TO MARKETS

BIOM Allchemix
Biomass to F&F Ingredients — All F&F Ingredients Consultancy

CUTTING

> 1,000,0000,000 MT

Softwood Fuel Cutting : >200 000 000 MT (wet)

Fuel wood 165,000,000 MT

Firewood

Softwood Non Fuel Cutting : > 800 000 000 MT (wet)
trees cut to feed saw mills & pulp mills

Cut timber, let dry 6 months

68.8 % biomass

Barky logs

Saw mills

Pulp mills

~30% dead biomass stay in forest, decay→ microorganisms→animal CO^2

Stumps & roots

17.2 % biomass

170,000 MT of stumps

Needles foliage

2.8 % biomass

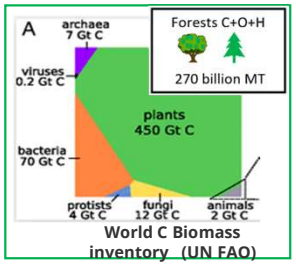
F&F <100 mt

Branches & tops

11.2% biomass

Cosmetics <500 mt

GLOBAL SOFTWOOD BIOMASS FLOW TO MARKETS



World C Biomass inventory (UN FAO)

Hardwood forests = 180 billion MT

Softwood forests = 90 billion MT

CUTTING

170,000 MT of stumps

Stump collection
: dead wood stumps removed from forest land

99.9% Decay in forest

Distillation

bioEnergy

Spent wood

Solvent extraction

<2000 mt WT Natural "wood"
Turpentine 50% alpha 5% beta

30% dark phenolic rosin >3,000 MT

Asphalt & construction

70% Wood Rosin >7,000 MT

Other esters wood Resin >5,000 MT

Glycerol Ester of Abietic acid ~2000 MT

Pine Resins 1,120,000 mt (Adhesives,inkt,tires, coatings, sealants,sizing…)

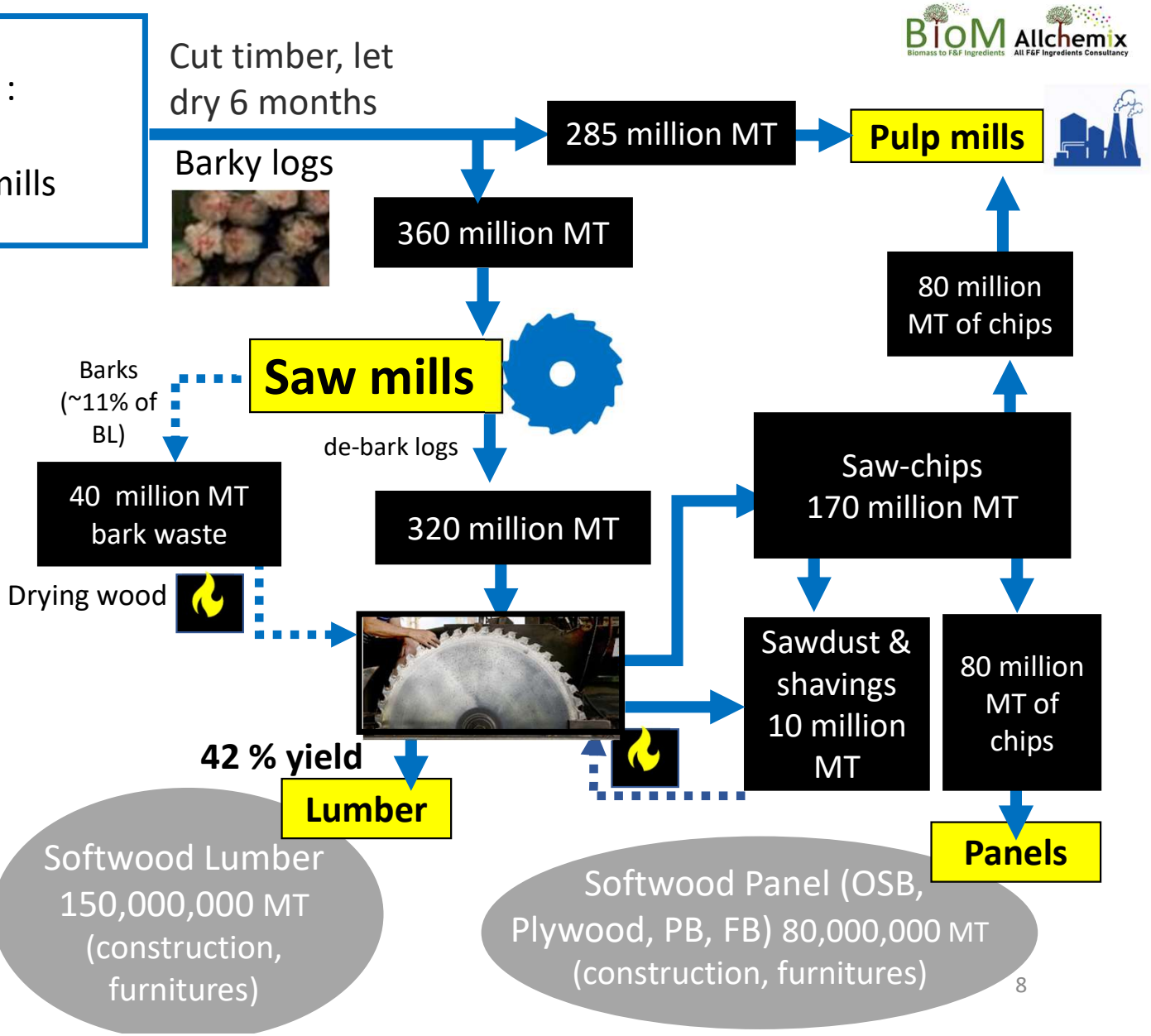
Beverages

Softwood Non Fuel Cutting :

> 800 000 000 MT (wet)

trees cut to feed saw mills & pulp mills

SAW MILLS



PULP MILLS

Pulp mills

waste bark 35 million MT

330 million MT of debarked wood

65 million MT

23% Other Pulp mills

MECHANICAL PULP MILLS
Rearrangement of fibers, no extraction of components

SEMI-MECHANICAL Chemo-Thermo MILLS CTMP
Rearrangement of fibers, no extraction of components

ORGANOSOLV
Cleaner tech, to be improved, Good cellulose and sulfur-free lignin separation

PULP
30,000,000 MT

25 million MT

7% Sulfite Pulp mills acidic digestion

SULFITE MILL
More for Spruce, less for Pine, weaker fibers, 41% yield, lignin separation, but sulfur

Na2SO3 impregnation Cooking

Separation of lignin from cellulose

BROWN LIQUOR

evaporating

Washing Bleaching

PULP
10,000,000 MT

Animal feed
(pellet binders, Ca Na electrolytes, gut agents)

Ligno-sulfonates
3,000,000 mt

Food
(filler, vanillin)

Construction
(concrete)
Agrochem
(dispersing agent)

240 million MT

70% KRAFT Pulp mills alkaline digestion

KRAFT PULP MILL
Cheapest,yield 43%, stronger fibers, but sulfur

NaOH + Na2S impregnation Cooking

Separation of lignin from cellulose

evaporating

Washing Bleaching

KRAFT PULP
strong cellulose
100,000,000 MT

Food
(filler)

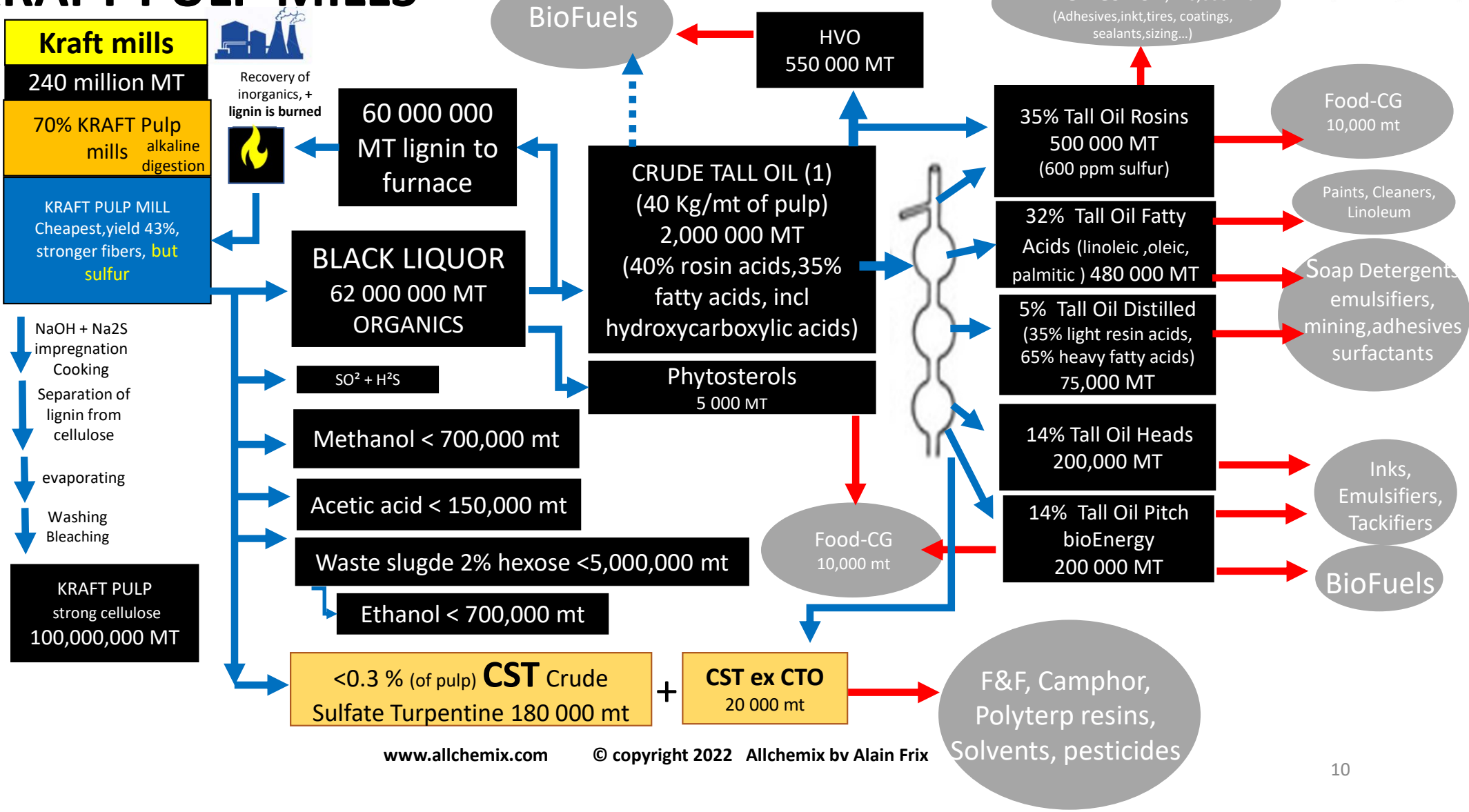
Pharma
(laxatives)

Methylcellulose
100,000 MT

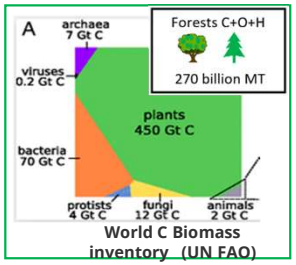
Pulp =Cellulose
Soft wood Paper
140 000 000 MT

ALL PULP
140,000,000 MT

KRAFT PULP MILLS



GLOBAL SOFTWOOD BIOMASS FLOW TO MARKETS



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CUTTING TAPPING

Tapping : access 260,000,000 MT biomass trees alive, only resin collected

Tapping is somehow sustainable

collect < 900,000 MT oleoresin, avg yield 4 Kg per tree times year

Distillation

~17% **GT** Natural "gum" Turpentine 150 000 mt

10% water

~70% Gum Rosins (90% resin acid) 650 000 MT

Bio chemicals

Biorefinery ????

?

Conifers dry biomass (average green biomass : 100% moisture content = 50% of weight is water)
42% cellulose (glucose long polymers) 3 xlonger than hardwoods
27% hemicelluloses net (crossed polymers various sugars)
28% lignin rigidity (polymers of phenylpropane units)
70% softwood VOC are terpenes, then hexanal..

> 1,000,0000,000 MT

Softwood Fuel Cutting : >200 000 000 MT (wet)

Softwood Non Fuel Cutting : > 800 000 000 MT (wet) trees cut to feed saw mills & pulp mills

-20% water

~30% dead biomass stay in forest, decay→ microorganisms→animal CO^2

Stumps & roots 17.2 % biomass

Needles foliage 2.8 % biomass

Branches & tops 11.2% biomass

Fuel wood 165,000,000 MT

F&F <100 mt

Cosmetics <500 mt

Cut timber, let dry 6 months

-20% water

Barky logs BL

68.8 % biomass

285,000,000 MT

360 million MT

Saw mills

Barks (~11% of BL)

de-bark logs

320,000,000 MT

40,000,000 MT waste bark

Drying wood

42 % yield

Lumber

Saw-chips 170,000,000 MT

Sawdust & shavings 10,000,000 MT

80 million MT of chips

Panels

Softwood Lumber 150,000,000 MT (construction, furnitures)

Softwood Panel (OSB, Plywood, PB, FB) 80,000,000 MT (construction, furnitures)

170,000 MT of stumps

Stump collection : dead wood stumps removed from forest land

Pulp mills

Barks waste bark 35 million MT

65 million MT

23% Other Pulp mills

MECHANICAL PULP MILLS Rearrangement of fibers, no extraction of components

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25 million MT

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Na2SO3 impregnation Cooking

acidic digestion

Separation of lignin from cellulose evaporating

BROWN LIQUOR

Washing Bleaching

Ligno-sulfonates 3,000,000 mt

PULP 10,000,000 MT

100,000 mt biofuel ?

240 million MT debarked wood

70% KRAFT Pulp mills

KRAFT PULP MILL Cheapest,yield 43%, stronger fibers, but sulfur

NaOH + Na2S impregnation Cooking

alkaline digestion

Separation of lignin from cellulose evaporating

Washing Bleaching

PULP strong cellulose 100,000,000 MT

50,000 mt to biofuel

200,000 MT Pitch to boiler

Recovery of inorganics, **+ lignin is burned**

60 000 000 MT lignin to furnace

BLACK LIQUOR 62 000 000 MT ORGANICS

$SO^2 + H^2S$

<0.3 % (of pulp) **CST** Crude Sulfate Turpentine 180 000 mt

Methanol < 700,000 mt

Acetic acid < 150,000 mt

Waste slugde 2% hexose <5,000,000 mt

Ethanol < 700,000 mt

fermentation

Animal feed (pellet binders, Ca Na electrolytes, gut agents)

Construction (concrete) Agrochem (dispersing agent)

Pulp =Cellulose Soft wood Paper 140 000 000 MT

Methylcellulose 100,000 MT

Pharma (laxatives)

Food (filler, vanillin)

Asphalt & construction

Biodiesel >500,000 MT

HVO 400 000 MT

60 % yield

30 %

CRUDE TALL OIL (1) (40 Kg/mt of pulp) 1,800 000 MT (40% rosin acids,35% fatty acids, incl hydroxycarboxylic acids)

Soap skimming +H2SO4 220503BD

2 000 000 MT Organics

Pine Resins 1,120,000 mt (Adhesives,inkt,tires, coatings, sealants,sizing...)

480,000 mt TOR rOsins

35% Tall Oil Rosins 500 000 MT (2) (600 ppm sulfur)

CST 20 000 mt

32% Tall Oil Fatty Acids (linoleic ,oleic, palmitic)500 000 MT

5% Tall Oil Distilled (35% light resin acids, 65% heavy fatty acids) 75,000 MT

14% Tall Oil Heads 200,000 MT

14% Tall Oil Pitch bioEnergy 200 000 MT

Phytosterols 5 000 MT

CST 200 000 mt

Soap Detergents emulsifiers, mining,adhesives surfactants

Inks, Emulsifiers, Tackifiers

Paints, Cleaners, Linoleum

F&F, Camphor, Polyterp, Solvents

Food-CG 10,000 mt

<2000 mt **WT** Natural "wood" Turpentine 50% alpha 5% beta

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30% dark phenolic rosin >3,000 MT

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Spent wood

bioEnergy

Glycerol Ester of Abietic acid ~2000 MT

Other esters wood Resin >5,000 MT

= Business driver
= By-product
= Chemical reaction
= Bioenergy

(1) Some hydroxycarboxylic acids found in CTO : α- and β-glucoisosaccharinic, xylosaccharinic, lactic, 3,4-dideoxypentonic, 2-hydroxybutanoic, and glycolic acids

(2)Resin acids :
- Abietic (35-52%)
- Dehydroabietic (4-27%)
- Palustric (10-12%)
- Isopimaric (1-12%)
- Neoabietic (4-10%)
- Pimaric (1-7%)
- Sandrarcopimaric (0-3%)

BIOM Biomass to F&F Ingredients — Allchemix All F&F Ingredients Consultancy

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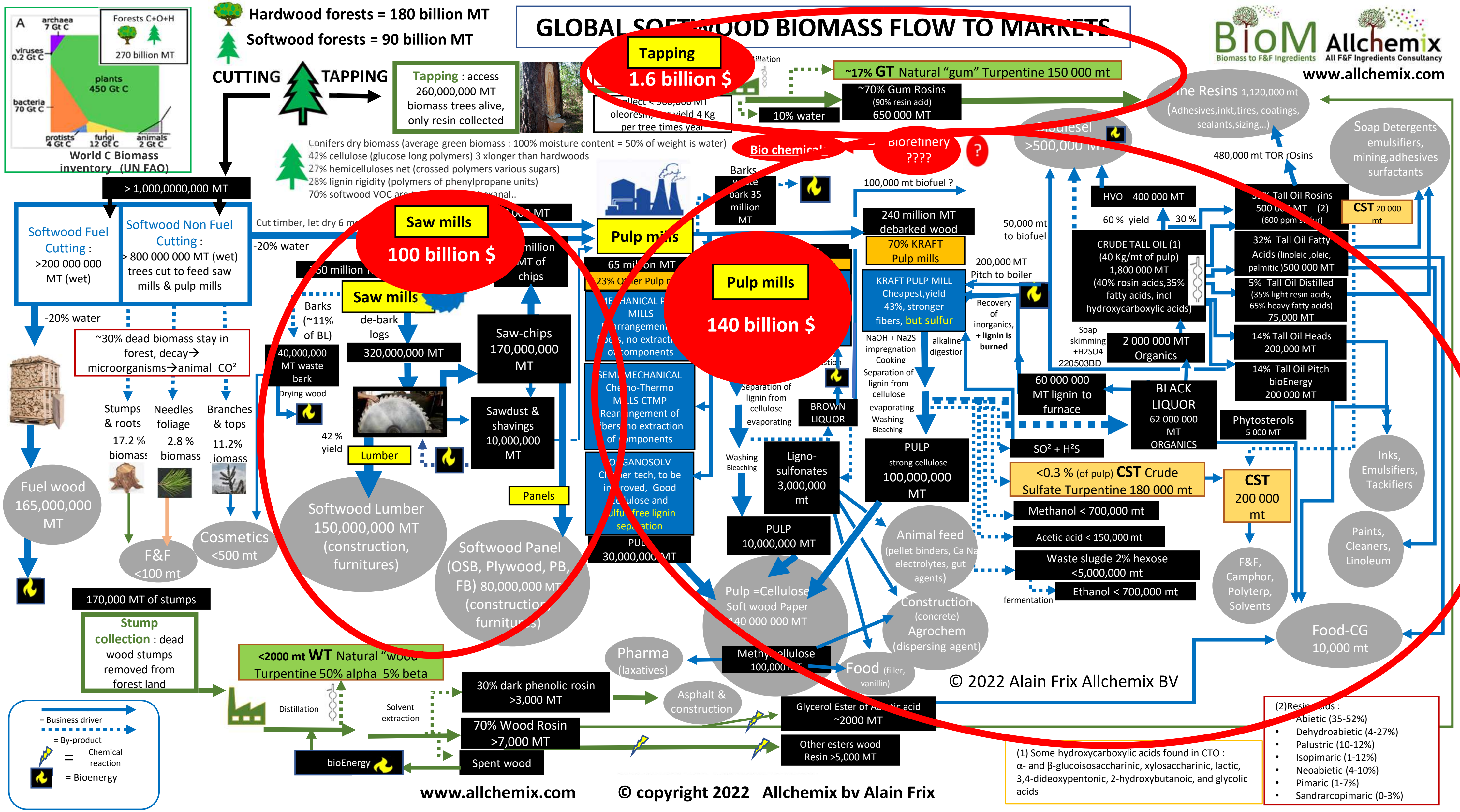

GLOBAL SOFTWOOD BIOMASS FLOW TO MARKETS
Tapping
1.6 billion $
Saw mills
100 billion $
Pulp mills
140 billion $
Biorefinery ????
Bio chemical
?
Hardwood forests = 180 billion MT
Softwood forests = 90 billion MT
CUTTING
TAPPING
Forests C+O+H
270 billion MT
archaea 7 Gt C
viruses 0.2 Gt C
plants 450 Gt C
bacteria 70 Gt C
protists 4 Gt C
fungi 12 Gt C
animals 2 Gt C
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Inks, Emulsifiers, Tackifiers
Paints, Cleaners, Linoleum
F&F, Camphor, Polyterp, Solvents
Food-CG 10,000 mt
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Spent wood
bioEnergy
Asphalt & construction
Glycerol Ester of Abietic acid ~2000 MT
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Fragrance & Flavour Ingredients

FLOW FROM PINE FORESTS

CONIFEROUS FORESTS DRIVERS :

SAW MILLS : 350,000,000 MT of wood → 230,000,000 MT of lumber and panels → CONSTRUCTION & FURNITURE

PULP MILLS : 280,000,000 MT of wood → 140,000,000 MT of cellulose → PAPER AND CARDBOARD

+ > 6,000,000 MT of by-products → Various Industries

PINE TAPPING: 1,000,000 MT of oleoresin through tapping tree alive → 650,000 MT Pine Rosins → RESINS

Lumber / Panels / Furnitures

Paper / Cardboard

Pine Resins

Turpentine
350,000 MT

Turpentine is one of smallest side streams in whole biomass chain, but with a wide range of applications

- Perfumes 
- Camphor 
- Terpene Resins 
- Agronomy 
- Solvents 

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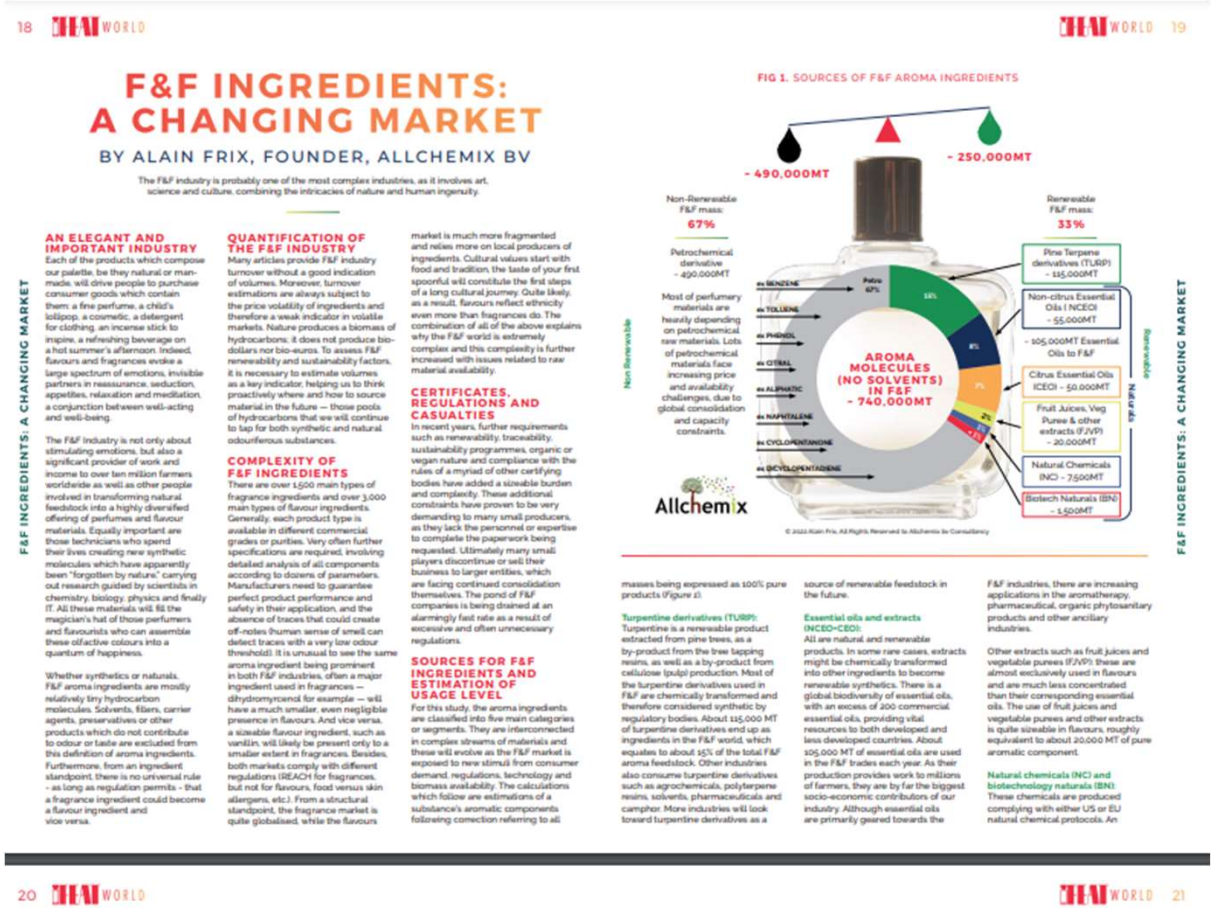
July 2022 https://ifeat.org/2022/07/ifeatworld-july-2022/

Also freely available on **www.allchemix.com**



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F&F INGREDIENTS: A CHANGING MARKET

F&F INGREDIENTS: A CHANGING MARKET

BY ALAIN FRIX, FOUNDER, ALLCHEMIX BV

The F&F industry is probably one of the most complex industries, as it involves art, science and culture, combining the intricacies of nature and human ingenuity.

AN ELEGANT AND IMPORTANT INDUSTRY

Each of the products which compose our palette, be they natural or man-made, will drive people to purchase consumer goods which contain them: a fine perfume, a child's lollipop, a cosmetic, a detergent for clothing, an incense stick to inspire, a refreshing beverage on a hot summer's afternoon. Indeed, flavours and fragrances evoke a large spectrum of emotions, invisible partners in reassurance, seduction, appetites, relaxation and meditation, a conjunction between well-acting and well-being.

The F&F industry is not only about stimulating emotions, but also a significant provider of work and income to over ten million farmers worldwide as well as other people involved in transforming natural feedstock into a highly diversified offering of perfumes and flavour materials. Equally important are those technicians who spend their lives creating new synthetic molecules which have apparently been "forgotten by nature," carrying out research guided by scientists in chemistry, biology, physics and finally IT. All these materials will fill the magician's hat of those perfumers and flavourists who can assemble these olfactive colours into a quantum of happiness.

Whether synthetics or naturals, F&F aroma ingredients are mostly relatively tiny hydrocarbon molecules. Solvents, fillers, carrier agents, preservatives or other products which do not contribute to odour or taste are excluded from this definition of aroma ingredients. Furthermore, from an ingredient standpoint, there is no universal rule - as long as regulation permits - that a fragrance ingredient could become a flavour ingredient and vice versa.

QUANTIFICATION OF THE F&F INDUSTRY

Many articles provide F&F industry turnover without a good indication of volumes. Moreover, turnover estimations are always subject to the price volatility of ingredients and therefore a weak indicator in volatile markets. Nature produces a biomass of hydrocarbons; it does not produce bio-dollars nor bio-euros. To assess F&F renewability and sustainability factors, it is necessary to estimate volumes as a key indicator, helping us to think proactively where and how to source material in the future — those pools of hydrocarbons that we will continue to tap for both synthetic and natural odouriferous substances.

COMPLEXITY OF F&F INGREDIENTS

There are over 1,500 main types of fragrance ingredients and over 3,000 main types of flavour ingredients. Generally, each product type is available in different commercial grades or purities. Very often further specifications are required, involving detailed analysis of all components according to dozens of parameters. Manufacturers need to guarantee perfect product performance and safety in their application, and the absence of traces that could create off-notes (human sense of smell can detect traces with a very low odour threshold). It is unusual to see the same aroma ingredient being prominent in both F&F industries, often a major ingredient used in fragrances — dihydromyrcenol for example — will have a much smaller, even negligible presence in flavours. And vice versa, a sizeable flavour ingredient, such as vanillin, will likely be present only to a smaller extent in fragrances. Besides, both markets comply with different regulations (REACH for fragrances, but not for flavours, food versus skin allergens, etc.). From a structural standpoint, the fragrance market is quite globalised, while the flavours market is much more fragmented and relies more on local producers of ingredients. Cultural values start with food and tradition, the taste of your first spoonful will constitute the first steps of a long cultural journey. Quite likely, as a result, flavours reflect ethnicity even more than fragrances do. The combination of all of the above explains why the F&F world is extremely complex and this complexity is further increased with issues related to raw material availability.

CERTIFICATES, REGULATIONS AND CASUALTIES

In recent years, further requirements such as renewability, traceability, sustainability programmes, organic or vegan nature and compliance with the rules of a myriad of other certifying bodies have added a sizeable burden and complexity. These additional constraints have proven to be very demanding to many small producers, as they lack the personnel or expertise to complete the paperwork being requested. Ultimately many small players discontinue or sell their business to larger entities, which are facing continued consolidation themselves. The pond of F&F companies is being drained at an alarmingly fast rate as a result of excessive and often unnecessary regulations.

SOURCES FOR F&F INGREDIENTS AND ESTIMATION OF USAGE LEVEL

For this study, the aroma ingredients are classified into five main categories or segments. They are interconnected in complex streams of materials and these will evolve as the F&F market is exposed to new stimuli from consumer demand, regulations, technology and biomass availability. The calculations which follow are estimations of a substance's aromatic components following correction referring to all masses being expressed as 100% pure products (Figure 1).

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FIG 1. SOURCES OF F&F AROMA INGREDIENTS

Turpentine derivatives (TURP): Turpentine is a renewable product extracted from pine trees, as a by-product from the tree tapping resins, as well as a by-product from cellulose (pulp) production. Most of the turpentine derivatives used in F&F are chemically transformed and therefore considered synthetic by regulatory bodies. About 115,000 MT of turpentine derivatives end up as ingredients in the F&F world, which equates to about 15% of the total F&F aroma feedstock. Other industries also consume turpentine derivatives such as agrochemicals, polyterpene resins, solvents, pharmaceuticals and camphor. More industries will look toward turpentine derivatives as a source of renewable feedstock in the future.

Essential oils and extracts (NCEO+CEO): All are natural and renewable products. In some rare cases, extracts might be chemically transformed into other ingredients to become renewable synthetics. There is a global biodiversity of essential oils, with an excess of 200 commercial essential oils, providing vital resources to both developed and less developed countries. About 105,000 MT of essential oils are used in the F&F trades each year. As their production provides work to millions of farmers, they are by far the biggest socio-economic contributors of our industry. Although essential oils are primarily geared towards the F&F industries, there are increasing applications in the aromatherapy, pharmaceutical, organic phytosanitary products and other ancillary industries.

Other extracts such as fruit juices and vegetable purees (FJVP): these are almost exclusively used in flavours and are much less concentrated than their corresponding essential oils. The use of fruit juices and vegetable purees and other extracts is quite sizeable in flavours, roughly equivalent to about 20,000 MT of pure aromatic component.

Natural chemicals (NC) and biotechnology naturals (BN): These chemicals are produced complying with either US or EU natural chemical protocols. An

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