NANOTECHNOLOGY APPLIED TO INDUSTRIAL PRODUCTS.

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-Introduction to Nanotechnology

Nanotechnology can be defined in a number of ways. For the purpose of this paper, nanotechnology is regarded as the study, creation, synthesis, manipulations, and applications of functional materials, devices and systems through control at the near-atomic, or nanometer, level The unit of nanometer derives its prefix nano from a Greek word meaning dwarf or extremely small. A nanometer is one-billionth of a meter; a sheet of paper is about 100,000 nanometers thick. One nanometer spans 3-5 atoms lined up in a row. By comparison, the diameter of a human hair is about five orders of magnitude larger than a nanoscale particle. Nanomaterials are not simply another step in miniaturization, but a different arena entirely; the nanoworld lies midway between the scale of atomic and quantum phenomena, and the scale of bulk materials. At the nanomaterial level, some material properties are affected by the laws of atomic physics, rather than behaving as traditional bulk materials do [1-3]

–Applications of Nanotechnology

In a recent report of the National Science Foundation to the President's Office of Science and Technology Policy it was stated that "Nanoscience and technology will change the nature of almost every human-made object in the next century".

So what are these nanothings that are going to change our lives?

Perhaps the best way to begin to convey possibilities is list topical areas that nanotechnology can contribute to the attainment of the United Nations Millenium Development Goals (MDGs) (Table 1 and Figure1). The top ten nanotechnology applications identified in Table 1 are a good starting point for defining the grand challenges to accelerate the use of these top nanotechnologies by less industrialized countries to meet critical sustainable development[1-3].

The future applications of nanotechnology will rely heavily on the commercial development of nanomaterials — metals, ceramics, and composite materials that are produced at the nanoscale. New materials are interesting and over the past decade, nanomaterials have been the subject of enormous interest. These materials, notable for their extremely small feature size, have the potential for wide-ranging industrial, biomedical, and electronic applications (3,8). Because of recent improvement in technologies to see and manipulate these materials, the nanomaterials field has seen a huge increase in funding from various sources including national and international foundations, and from collaboration among nanotechnology initiatives in industrialized and developing countries.

-Nanomaterials

The variety of nanomaterials is great, and their range of properties and possible applications appear to be enormous, from extraordinarily tiny electronic devices, including miniature batteries, to biomedical uses, and as packaging films, superabsorbants, components of armor, and parts of automobiles [9]. It is clear that researchers are merely on the threshold of understanding and development, and that a great deal of fundamental work remains to be done.

These nanomaterials are so different and so intriguing due to their extremely small feature size is of the same scale as the critical size for physical phenomena - for example, the radius of the tip of a crack in a material may be in the range 1-100 nm. The way a crack grows in a larger-scale, bulk material is likely to be different from crack propagation in a nanomaterial where crack and particle size are comparable.

Fundamental electronic, magnetic, optical, chemical, and biological processes are also different at this level [10] Where proteins are 10-1000 nm in size, and cell walls 1-100 nm thick(Figure 2), their behavior on encountering a nanomaterial may be quite different from that seen in relation to larger-scale materials. Nanocapsules and nanodevices may present new possibilities for drug delivery, gene therapy, and medical diagnostics [9,10].

-The effect of surfaces and interfaces on the nanomaterials behavior

Surfaces and interfaces are also important in explaining nanomaterial behavior. In bulk materials, only a relatively small percentage of atoms will be at or near a surface or interface (like a crystal grain boundary). In nanomaterials, the small feature size ensures that many atoms, perhaps half or more in some cases, will be near interfaces. Consider, for example, that a 3 nm iron particle has 50% of its atoms on the surface, whereas a 10 nm particle has just 20% on the surface, and a 30 nm particle only 5 % [10] Surface properties are much different at the nanoscale, and quantum properties dominate. Increased surface areas of nanoparticles can lead to increased cellular reactivity, and increased bioavailability to increased toxicity. Lower effective doses of nanomaterials could mean toxic effects at lower doses.

-Nanocomposites

Based on polymeric materials, there are several varieties of polymeric nanocomposites, but the most commercially advanced are those that involve dispersion of small amounts of nanoparticles in a polymer matrix [11]. Those most humble of materials, clays, have been found to impart amazing properties. For example, adding such small amounts as 2% by volume of silicate nanoparticles to a polyimide resin increases the strength by 100%. Addition of nanoparticles not only improves the mechanical properties, but also has been shown to improve thermal stability, in some cases allowing use of polymer-matrix nanocomposites an additional 100 degrees Centigrade above the normal service conditions. Clay/polymer nanocomposites have been considered as matrix materials for fiber-based composites destined for aerospace components. Aircraft and spacecraft components require lightweight materials with high strength and stiffness, among other qualities.

Others have examined the electrical properties of nanocomposites, with an eye to developing new conductive materials. The use of polymer-based nanocomposites has been expanded to anti-corrosion coatings on metals, and thin-film sensors. Their photoluminescence and other optical properties are being explored. Polymer-matrix nanocomposites can also be used to package films, an application which exploits their superior barrier properties and low permeability. Polymer-matrix nanocomposites does not require exotic approaches to synthesis and processing , and can be prepared quite readily.

The introduction of inorganic nanoparticles as a additive into polymer system has resulted in polymer nanocomposites exhibiting multifunctional properties. Clay/polymer nanocomposites have been made by subjecting a clay such as montmorillonite to ion exchange or other pretreatment, then mixing the particles with polymer melts. The low volume fraction of reinforcement particles allows the use of well-established and well-understood processing methods, such as extrusion and injection molding. Ease of processing and forming may be one explanation for the rapidly expanding applications of the materials [11]. Automotive companies, in particular, have quickly adopted nanocomposites in large-scale applications, including structural parts of vehicles.

Carbon nanotubes are object of a tremendous research effort [3,11]. Nanoparticles of carbon - rods, fibers, tubes with single walls or double walls, open or closed ends, and straight or spiral forms--have been synthesized over the last decade. There is good reason to devote so much effort to them: carbon nanotubes have been shown to have unique properties, stiffness and strength higher than any other material, for example, as well as extraordinary electronic properties[3,11]. Carbon nanotubes are reported to be thermally stable in vacuum up to 2800 degrees Centigrade, to have a capacity to carry an electric current a thousand times better than copper wires, and to have twice the thermal conductivity of diamond (which is also a form of carbon). Carbon nanotubes are used as reinforcing particles in nanocomposites, but also have many other potential applications. They could be the basis for a new era of electronic devices smaller and more powerful than any previously envisioned. Nanocomputers based on carbon nanotubes have already been demonstrated.

It is not so amazing, then, that government bodies, companies, and university researchers are joining forces or competing to synthesize, investigate, produce, and apply these amazing nanomaterials. For example, the 2008 Budget provides U$1.5 billion for the NNI , more than triple the estimated U$ 464 million spent in 2001[12], and also several developing countries have launched nanotechnology initiatives in order to strengthen their capacity and sustain economic growth [13]. India's Department of Science and Technology will invest $20 million over the next five years (2004–2009) for their Nanomaterials Science and Technology Initiative [14,15]. The number of nanotechnology patent applications from China ranks third in the world behind the United States and Japan [16]. In Brazil, the projected budget for nanoscience during the 2004–2007 period is about $25 million, and three institutes, four networks, and approximately 300 scientists are working in nanotechnology [3,4,7,17]. The South African Nanotechnology Initiative (http:⁄⁄www.sani.org.za) is a national network of academic researchers involved in areas such as nanophase catalysts, nanofiltration, nanowires, nanotubes, and quantum dots. Other developing countries, such as Thailand, the Philippines, Chile, Argentina, and Mexico, are also pursuing nanotechnology [13].

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Table 1. Correlation between the Top Ten Applications of Nanotechnology for Developing Countries and the UN Millennium Development Goals

Ranking (Score)	Applications of Nanotechnology	Examples	Comparison with the MDGs
1 (766)[a]	Energy storage, production, and conversion	Novel hydrogen storage systems based on carbon nanotubes and other lightweight nanomaterials Photovoltaic cells and organic light-emitting devices based on quantum dots Carbon nanotubes in composite film coatings for solar cells Nanocatalysts for hydrogen generation Hybrid protein-polymer biomimetic membranes	VII
2 (706)	Agricultural productivity enhancement	Nanoporous zeolites for slow-release and efficient dosage of water and fertilizers for plants, and of nutrients and drugs for livestock Nanocapsules for herbicide delivery Nanosensors for soil quality and for plant health monitoring Nanomagnets for removal of soil contaminants	I, IV, V, VII
3 (682)	Water treatment and remediation	Nanomembranes for water purification, desalination, and detoxification Nanosensors for the detection of contaminants and pathogens Nanoporous zeolites, nanoporous polymers, and attapulgite clays for water purification Magnetic nanoparticles for water treatment and remediation TiO_2 nanoparticles for the catalytic degradation of water pollutants	I, IV, V, VII
4 (606)	Disease diagnosis and screening	Nanoliter systems (Lab-on-a-chip) Nanosensor arrays based on carbon nanotubes Quantum dots for disease diagnosis Magnetic nanoparticles as nanosensors Antibody-dendrimer conjugates for diagnosis of HIV-1 and cancer Nanowire and nanobelt nanosensors for disease diagnosis Nanoparticles as medical image enhancers	IV, V, VI
5 (558)	Drug delivery systems	Nanocapsules, liposomes, dendrimers, buckyballs, nanobiomagnets, and attapulgite clays for slow and sustained drug release systems	IV, V, VI
6 (472)	Food processing and storage	Nanocomposites for plastic film coatings used in food packaging Antimicrobial nanoemulsions for applications in decontamination of food equipment, packaging, or food Nanotechnology-based antigen detecting biosensors for identification of pathogen contamination	I, IV, V
7 (410)	Air pollution and remediation	TiO_2 nanoparticle-based photocatalytic degradation of air pollutants in self-cleaning systems Nanocatalysts for more efficient, cheaper, and better-controlled catalytic converters Nanosensors for detection of toxic materials and leaks Gas separation nanodevices	IV, V, VII
8 (366)	Construction	Nanomolecular structures to make asphalt and concrete more robust to water seepage Heat-resistant nanomaterials to block ultraviolet and infrared radiation Nanomaterials for cheaper and durable housing, surfaces, coatings, glues, concrete, and heat and light exclusion Self-cleaning surfaces (e.g., windows, mirrors, toilets) with bioactive coatings	VII
9 (321)	Health monitoring	Nanotubes and nanoparticles for glucose, CO_2, and cholesterol sensors and for in-situ monitoring of homeostasis	IV, V, VI
10 (258)	Vector and pest detection and control	Nanosensors for pest detection Nanoparticles for new pesticides, insecticides, and insect repellents	IV, V, VI

[a] The maximum total score an application could receive was 819.

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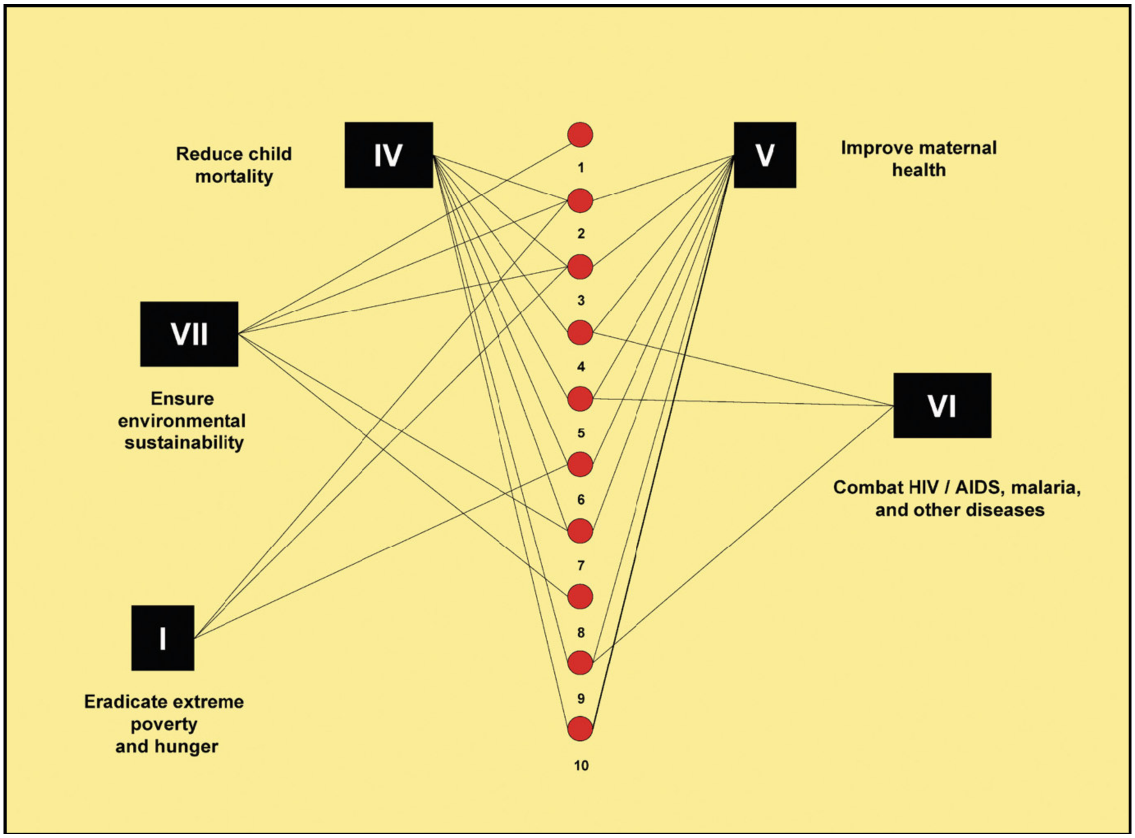

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Figure 1. Comparison between the Millennium Development Goals and the Nanotechnologies Most Likely to Benefit Developing Countries in the 2004–2014 Period.

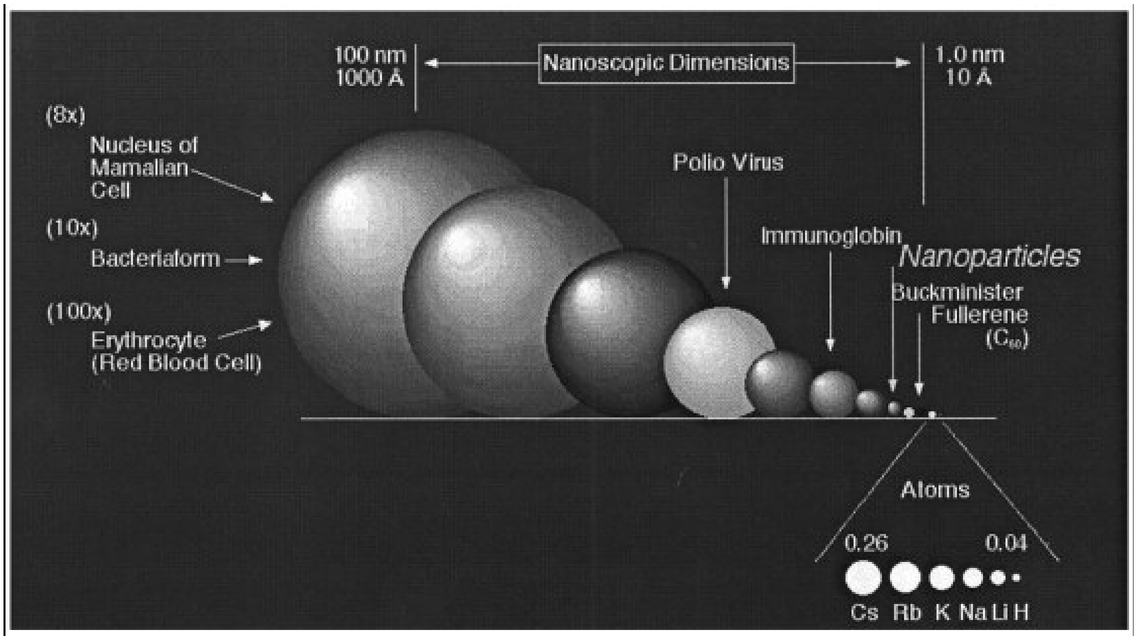

Figure 2. Size comparisons of nanocrystal with bacteria, viruses, and molecules. From reference 10.

RESEARCH, COMMERCIALIZATION AND UTILIZATION OF SOYBEAN INDUSTRIAL PRODUCTS IN THE UNITED STATES

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The United Soybean Board (USB) is made up of 68 farmer-directors who oversee the investments of the soybean checkoff on behalf of all U.S. soybean farmers. Checkoff funds are invested in the areas of animal utilization, human utilization, industrial utilization, industry relations, market access and supply.

The latest U.S. Department of Agriculture report projects that U.S. soybean farmers harvested 75 million acres in 2006 which produced slightly less than 3.2 billion bushels of soybeans. About 1.1 billion bushels is projected to be exported. It is also projected that 1.8 billion bushels will be crushed resulting in 20.2 billion pounds of soybean oil and 42.4 million short tons of soybean meal. Most of the soybean meal is utilized for livestock production. An excess of 2.7 billion pounds of soybean oil is projected for the end of the current marketing year (August 31, 2007).

USB is committed to funding the research, development and commercialization of new industrial uses for soybeans. One mission of the USB is to create new soybean demand through the discovery, development and introduction of new industrial soybean-based products and applications.

Biobased products can help protect and preserve the environment. At the same time, they can create a safer, healthier workplace. They can help cut air and water pollution, reduce the generation of hazardous waste, and decrease the use of potentially toxic substances. However, the resulting product must perform as well or better than the product it is replacing and costs in use must be equal or less.

To quantify the environmental impact of soy based industrial products, a life cycle assessment was performed on a soy polyol used in making polyurethanes. This was then compared to a petroleum based polyol using a model developed by the US National Institute of Science and Technology known as the BEES (Building Environmental and Economic Sustainability) model. When the soy polyol was compared to the petroleum product using the US Environmental Protection Agency's impact criteria, the soy product showed lower or equivalent impacts in a majority of the areas such as smog formation, global warming, eutrophication, fuel energy use, environmental toxicity and human toxicity. It was higher in some areas such as water intake but received a significantly lower, and therefore favorable, overall score.

Rising oil prices are causing many industrial companies to seriously consider alternatives to petrochemicals. New soy-based products are quickly gaining popularity as USB spreads the word about the many benefits of soy to industry leaders and researchers. For the past decade, USB has helped develop many successful new uses. Research to find new applications for these products continues in an effort to utilize more U.S. soybeans.

Since 1999/00, estimated industrial use of soybean oil in the US, not including biodiesel, has risen from 500 million pounds to over 800 million pounds in 2005/06. While much of this utilization came from traditional oleochemical products such as soaps, surfactants, industrial amines and alkyd resins, the majority of the growth is attributed to newer uses such as plastics, inks, solvents and other uses which began to attain significant levels of utilization during the period.

The USB has identified five primary target areas that hold great potential for soy-based products: adhesives (primarily wood adhesives); solvent, water-borne and powder coatings and printing inks; lubricants, from engine oils to railway lubricants; plastics, particularly rigid and flexible polyurethanes; and specialty products, which range from paint strippers, and industrial cleaners to mosquito control agents, transformer oils, cosmetics and hand lotions.

In the past few years, new technologies have been developed that use soy in the manufacturing of plastics. Replacing a portion of petrochemical ingredients, soybean oil is mixed with an isocyanate to create a polyol used for manufacturing rigid and flexible polyurethane foam. Soybean oil is also an ingredient in the development of a reactive thermoset resin used in molded composites.

SOY-BASED POLYOL

REPLACEMENT POTENTIAL (M LBS.)

Product	Market Size (2004A) (mil. Lb.)	Soy Polyol Potential (2009E) (mil. lb)
Construction	770	200
Transportation	860	100
Carpet	356	60
Furniture, Bedding	743	100
Other*	826	190
Total	3,555	650

*Other: footwear, marine, packaging, foundry, machinery, and industrial, misc.

Methyl soyate, the main ingredient in soy-based solvents, is another example of how biobased products enhance environmental and worker safety. Methyl soyate is low in volatile organic compounds (VOCs) and does not generate Hazardous Air Pollutants (HAPs). It can reduce hazardous waste generation and lower costs for disposal, insurance and regulatory reporting. Testing shows that soy-based solvents may improve fire safety due to a very high flash point. They are readily biodegradable and lower in toxicity than most common solvents. Methyl soyate offers good potential as a partial industrial solvent replacement for use in parts cleaning, paint and ink removal and formulated specialty consumer products.

METHYL SOYATE (SME)
SOLVENT REPLACEMENT POTENTIAL (M LBS.)

Product	2006 Total	2006 Potential Replacement
TCE(trichloroethylene)	220	35
Perc(perchloroethylene)	375	55
MeCl(methylene chloride)	200	70
MEK(methyl ethyl ketone)	380	65
D'Limonene	100	50
Other Solvents	500	100
Total	1,775	375

Other examples of products that enhance environmental and worker safety are soy-based two-cycle engine oils and metal working fluids. The two-cycle engine oil is readily biodegradable, virtually nontoxic and exceeds the performance requirement of the International Organization for Standardization (ISO) global specification, the world's toughest standard for this type of lubricant. Soy-based metal working fluids emit fewer harmful emissions than petrochemical-based oil for increased worker safety.

Wood adhesives made from soybeans have been in existence for over seven decades. However, with the introduction of phenol- and urea-based adhesives in the 1930s, soy adhesives were replaced. Recent government regulations placed on the lumber industry have mills looking at green alternatives to these chemical-based adhesives and successful new formaldehyde-free soy based wood adhesives are being introduced.

The overall market for paints and coatings in the United States tops 1.2 billion gallons, although the recent past has seen a downward trend in soy use. Soybean oil continues to be used in the production of alkyd paints, but these paints have lost market share to waterborne paints. Waterborne paints are less expensive and lower in odor than alkyd paints, two characteristics that are important to consumers. To combat this, the USB is supporting research to develop new soy resins that can be made into coatings with water or lower levels of solvents.

The printing industry has been using soybean oil-based inks since the early 1990s. In fact, more than 95 percent of daily newspapers in the United States are printed with soy ink.

The issue of developing new industrial uses for soybean meal and its derivatives such as soy flour, soy protein concentrates and soy protein isolates has been, and will continue to be, considered and investigated. Anticipated increases in soybean oil demand resulting from biodiesel and other industrial uses, along with rising prices for competitive petrochemicals has driven an expanded effort to increase industrial utilization of meal and protein.

Additional information on the production, commercialization and utilization of soybean products in the United States can be found on the USB website at unitedsoybean.org/newuses

BIODIESEL NA PETROBRAS

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Palavras-chave: Biodiesel; Desenvolvimento; PETROBRAS; Petróleo; Diesel; Fonte Renovável

Introdução

Já faz alguns anos que a humanidade percebeu que as alterações que ela vinha provocando na natureza em nome do seu desenvolvimento estão provocando mudanças irreversíveis ao meio ambiente, as quais podem torná-lo inóspito à vida humana no futuro. O efeito estufa é uma das principais respostas da natureza às agressões do homem e é devido, principalmente, à emissão de óxidos de carbono provenientes de processos de combustão.

Óxidos de carbono são formados na queima de combustíveis fósseis na geração de energia, em especial de derivados de petróleo. Uma alternativa a este processo é a busca por combustíveis que possam gerar energia sem provocar grandes agressões ao meio ambiente e esse desafio é o que passa todas as empresas de energia comprometidas com o desenvolvimento sustentável do planeta. A PETROBRAS, como uma dessas empresas, tem esse objetivo dentro do seu plano estratégico e vai investir US$ 700 milhões entre 2007 e 2011 para o desenvolvimento energético de fontes renováveis e biocombustíveis.

A participação de fontes renováveis e mais limpas, como a biomassa (biocombustíveis), é cada vez maior na matriz energética mundial. Essa mudança nas fontes de energia se dará por dois fatores principais: a maior consciência ambiental e a escassez das fontes não renováveis de energia.

Vantagens do uso do Biodiesel

Entre as fontes de energia ecologicamente corretas pode-se destacar o biodiesel, pois além de diminuir a emissão de gases do efeito estufa, reduz a emissão de outros contaminantes, pode gerar emprego e renda em comunidades socialmente desfavorecidas, contribui para a segurança energética do país no longo prazo e reduz a importação de óleo diesel feita pelo Brasil.

As emissões dos motores a ciclo diesel estão relacionadas com a qualidade da queima e a combustão nesses motores se inicia pela auto-ignição das gotículas do óleo diesel injetadas no motor e, portanto, é bastante complexa.

O teor de enxofre, por exemplo, influencia diretamente as emissões de materiais particulados do motor. O biodiesel está praticamente isento de compostos de enxofre, assim como de compostos aromáticos, e contém cerca de 11% de oxigênio em peso. Estas características indicam que as emissões de gases contaminantes e produtos cancerígenos serão menores com a utilização do biodiesel. Essas análises consideram todo o ciclo de vida do combustível e não somente o uso final do produto.

No ciclo de vida do biodiesel há a redução de 95% das emissões de gases do efeito estufa, 78% nas emissões de CO_2, 48% nas emissões de CO, 47% nas emissões dos materiais particulados e hidrocarbonetos e a eliminação quase que total das emissões de compostos de enxofre. A única desvantagem é o aumento de 10% nas emissões de óxidos de nitrogênio.

Um dos objetivos principais do Programa de Biodiesel do Governo Federal é a geração de empregos, em especial na agricultura. Isto se deve à sua matéria-prima: grãos de oleaginosas.

Além da criação de emprego e renda e das vantagens ambientais, o biodiesel tem algumas vantagens técnicas em relação ao diesel mineral, como:

- Maior lubricidade; a diminuição da quantidade de enxofre no diesel mineral devido a restrições ambientais prejudica a sua lubricidade e a adição de biodiesel age no sentido inverso, melhorando a lubricidade, ainda que isento de compostos de enxofre;
- Maior índice de cetano;
- Melhor ponto de fulgor.

Entretanto, também apresenta algumas desvantagens como problemas de desempenho a baixas temperaturas e menor estabilidade em relação ao diesel.

Brasil e o Biodiesel

O Brasil tem um grande potencial de se sobressair no cenário mundial de biodiesel, pois pode se beneficiar de sua experiência em biocombustíveis: desde a década de 70 o etanol é um dos principais combustíveis da matriz energética nacional. Além disso, a sua larga extensão territorial, seu clima e a capacidade de cultivar diversas oleaginosas em quase todo o país fazem do biodiesel um combustível de grande potencial para o Brasil.

Uma das coisas que a experiência do álcool nos pode ensinar é que o custo da produção de biocombustíveis tende a cair à medida que os anos passam. De1980 até 1998 o custo caiu de US$ 105/bbl para cerca de US$ 30/bbl.

Em 2004 foi assinado o decreto que autorizava o uso de biodiesel no Brasil, viabilizando a sua utilização, visto que este combustível pode contribuir para a solução de questões fundamentais para o país, como a geração de emprego, inclusão social, redução na emissão de poluentes, diminuição das disparidades regionais de desenvolvimento e da dependência de importação de diesel. Em outras palavras, pode trazer benefícios sociais, econômicos, ambientais e estratégicos.

O óleo diesel é o combustível mais utilizado no país, principalmente no transporte de passageiros e carga (corresponde a 54,5% do consumo nacional de combustíveis veiculares) e aproximadamente 5% de todo diesel consumido é importado.

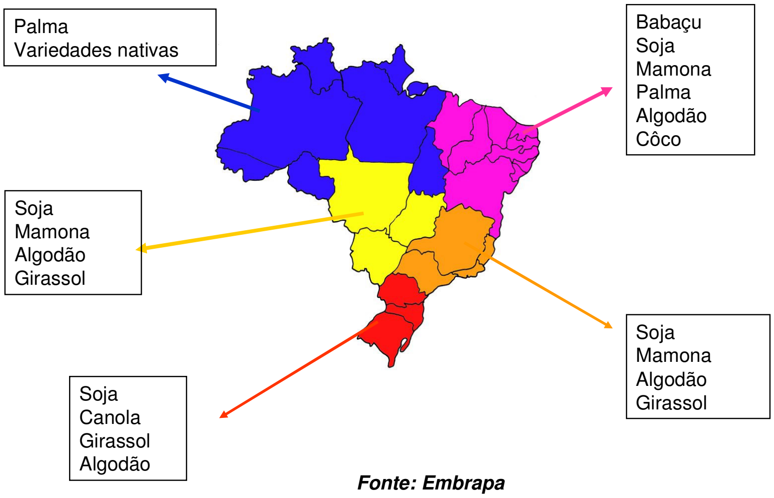
A partir de 2005 e até 2007 o Governo autoriza a mistura B2, porém, a partir de 2008 esta mistura será compulsória. Essa regra valerá até o final de 2012, pois a partir de 2013 a mistura B5 será obrigatória. Há uma estimativa de que o uso da mistura B2 gera um mercado de cerca de 840 milhões de litros/ano de biodiesel a partir de 2008 e com a mistura B5 esse mercado se ampliará a aproximadamente 2,5 bilhões de litros/ano em 2013. O marco regulatório que autoriza o uso comercial de biodiesel no país considera a diversidade de oleaginosas disponíveis, a garantia de provisão e de qualidade, a competitividade frente aos demais combustíveis e a política de inclusão social. As regras permitem a produção a partir de diferentes oleaginosas e rotas sintéticas.

Com o objetivo de incentivar a produção de biodiesel e sua utilização no país antes de 2008, a Agência Nacional de Petróleo, Gás Natural e Biocombustíveis (ANP) realizou 5 leilões para compra de biodiesel. Nesses leilões o volume ofertado foi sempre superior ao volume comprado e sempre com deságio que variaram de 1 a 8%. O preço médio do último leilão, realizado em fevereiro deste ano, foi de R$ 1,862/l.

A figura 1 mostra as oleaginosas que podem ser produzidas nas diferentes regiões do Brasil. É possível observar a grande diversidade de oleaginosas com potencial de utilização, conferindo uma flexibilidade importante para a produção de biodiesel.

A combinação dessa variedade de matérias-primas com a grande extensão de terras faz do biodiesel um combustível com grande potencial em nosso país. O Brasil tem mais de 850 milhões de hectares e perto de 10% do país é de áreas cultiváveis e livres, ou seja, há muito mais terra livre para o plantio de oleaginosas que o necessário para viabilizar o programa de biodiesel.

Por ser um programa realmente nacional e com grande disponibilidade de terra, usinas de biodiesel são construídas em todo o país. São cerca de 100 plantas espalhadas nas cinco regiões do Brasil, algumas destas plantas já estão produzindo enquanto outras ainda estão em fase de projeto. Cada planta usa um conjunto peculiar de insumos adequados à sua realidade regional.



Fonte: Embrapa

Figura 1: Potencial do Brasil na produção de oleaginosa

Será assim também com as plantas que estão sendo construídas pela PETROBRAS. Cada uma será suprida com as matérias-primas mais adequadas e na quantidade mais propícia. O plano estratégico da empresa prevê a produção de 855 milhões l/ano de biodiesel em 2011.

No final deste ano a PETROBRAS iniciará a sua produção de biodiesel nas 3 unidades que estão em construção no momento: em Quixadá (CE), Candeias (BA) e Montes Claros (MG). Serão utilizados óleo de mamona, algodão, palma e soja e gordura animal como insumo dessas plantas. Esses 3 empreendimentos consumirão R$ 227 milhões em investimentos.

Aspectos Tecnológicos

A cadeia produtiva do biodiesel se inicia com a plantação das oleaginosas e sua colheita. Os grãos são esmagados para a extração do óleo, produzindo também o farelo que pode ser utilizado para ração animal. O óleo vegetal é pré-tratado para corrigir sua acidez e segue para a planta de transesterificação, onde reage com o metanol para produzir biodiesel e glicerina. O primeiro é misturado ao diesel na quantidade desejada para seguir aos postos e ser vendido no varejo, enquanto que a glicerina pode ser utilizada como insumo de algumas indústrias como a de cosméticos, química, de alimentos, etc.

Como dito acima, a produção convencional de biodiesel é feita pela reação de transesterificação entre o óleo vegetal e um álcool. Essa reação transforma as moléculas de triglicerídeos do óleo vegetal em 3 moléculas de ésteres (biodiesel), formando também glicerina como co-produto. Cada 10 kg de óleo vegetal produzem cerca de 10 kg de biodiesel e 1 kg de glicerina. Essa glicerina, para ser colocada nos mercados hoje existentes, necessita de purificação e, mesmo assim, encontrará resistência, pois a quantidade que será produzida é superior ao mercado atual de glicerina no Brasil. Sendo assim, faz-se necessário encontrar novos usos para a glicerina de forma a agregar valor à cadeia do biodiesel.

A PETROBRAS, através do seu excelente Centro de Pesquisas e Desenvolvimento Leopoldo Américo Miguez de Mello (Cenpes), desenvolveu um processo inovador de produção de biodiesel que, ao invés de partir do óleo vegetal, parte do grão da oleaginosa. Esse grão é misturado com etanol para produzir o biodiesel juntamente com glicerina e a polpa como co-produtos. Esse processo apresenta algumas vantagens em relação ao processo convencional, dentre elas a utilização de etanol ao invés de metanol e a supressão da etapa de esmagamento de grãos. A quantidade de biodiesel obtida por esse processo é praticamente a mesma que a produzida pelo método convencional. Esta tecnologia é dominada somente pela PETROBRAS, que tem uma unidade piloto em Guamaré (RN), onde também há uma unidade piloto que utiliza o processo convencional. Estas duas plantas pilotos têm capacidade conjunta de 15.900 m^3/ano e geram emprego para aproximadamente 5.000 famílias.

Comercialização

Apesar de ainda não produzir biodiesel, a PETROBRAS já o comercializa como mistura B2 em mais de 3.800 de seus postos e em cerca de 1.200 cidades brasileiras. O biodiesel usado nessa mistura provém dos leilões realizados pela ANP mencionados acima.

Através do estudo dos erros e acertos da indústria de biodiesel, alguns fatores críticos para o sucesso. O primeiro desses fatores é a disponibilidade de matéria-prima – óleo vegetal e semente – o que significa que é indispensável que haja investimento em esmagamento e víveres para produção de sementes de boa qualidade. O aumento de produção está ligado a pesquisas para a melhora da produtividade agrícola. Além disto, é necessário que se tenha matéria-prima de qualidade, pois somente assim o produto final – o biodiesel – também terá qualidade. Entretanto, não basta que o biodiesel saia da planta industrial dentro das especificações, mas que a qualidade do produto nos postos seja a desejada. Porém, nada disso será efetivo se os motores a diesel não tiverem um desempenho similar utilizando biodiesel e diesel.

Outro fator decisivo para o desenvolvimento do biodiesel no exterior foi uma tributação inferior à do diesel, pois seu custo de produção é maior. Também é importante, para sua viabilidade econômica, desenvolver novos usos para a glicerina e ter um processo com produtividade e escala razoáveis, de forma a baixar o seu custo de produção.

Entretanto, o mais importante de todos os fatores de sucesso é a sensibilização e motivação da sociedade para que entenda a importância social, ambiental e econômica do programa de biodiesel para o país. Se a sociedade não perceber essa importância, o programa estará fadado ao fracasso mesmo que os outros fatores sejam atendidos.

Conclusão

O Programa Nacional de Biodiesel se baseia em 3 pilares básicos: desenvolvimento social, melhoria ambiental e vantagem econômica para o país e para a sociedade. Qualquer projeto que tenha estes pilares em sua concepção é intrinsecamente sustentável, ou seja, não depende de fatores externos ao projeto para obter sucesso, pois todos seus atores obtêm benefícios.

Como o programa é auto-sustentável, mesmo que ainda esteja iniciando, tem uma grande potencialidade de alcançar o sucesso. É por isso que a PETROBRAS, como uma empresa de energia, entra na cadeia de biodiesel com o objetivo de contribuir para este sucesso do programa e tornar o biodiesel um dos principias combustíveis da matriz energética brasileira no futuro.

PRODUCTION, COMMERCIALIZATION AND UTILIZATION OF SOYBEAN INDUSTRIAL PRODUCTS IN EUROPE

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KEYWORDS: soybean production, soybean imports, soybean exports, industrial use of soybean

INTRODUCTION

It is a European certitude that the non-food industrial uses of agricultural feedstocks will induce economic, social, and environmental well-being. The reinforcement of old and new markets for petrol-substitution products generates new research works and scientific knowledge is therefore created.

The EU agricultural policy was reformed on May 1, 2004 when 10 new Member Nations integrated the European Union. The non-food agricultural products were particularly encouraged and the conditions required for their use and development were established.

The aim of this article is to present the European situation of soybean and soybean oil general and the industrial uses of the latter in particular.

1. SOYBEANS

The almost 400 millions tons♦ (Mt) production of oleaginous in the world is distributed as shown in Figure 1.

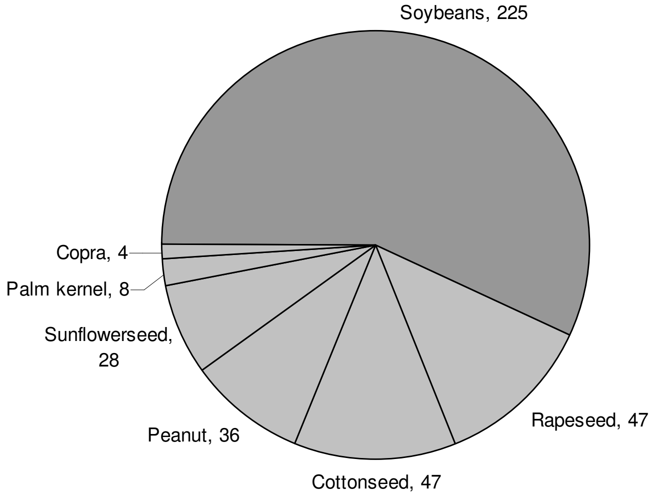

Figure 1: World Production (million tons) of oleaginous in 2004. Sources: PROLEA and USDA.

♦ "Tons" refers to <u>metric</u> tons (1000 kg)

Soybeans represent the highest production (225 million tons, 57% of the total). The main producers are USA (86 Mt), Brazil (62 Mt), Argentina (37 Mt), and China (18 Mt). These four countries cumulate 90% of the total production (Table 1).

	USA	Brazil	Argentina	China	India	Others	Total
2000/01	75	39	27	15	5	13	175
2001/02	79	43	30	15	5	12	184
2002/03	75	52	35	17	4	14	197
2003/04	67	50	32	16	7	14	185
2004/05	86	62	37	18	7	16	225

Table 1: World production of soybeans in million tons. Distribution by countries and years 2000-2005.
Source: Oil world.

The European Union, with 25 Member Nations (EU-25), produced only 0.78 Mt of soybeans in 2004, which corresponds to less than 0.4% of the world production (Table 2).

	Area (thousand Hectares)			**Yield** (tons/ha)			**Production** (Thousand Tons)		
	2003	**2004**	**2005**	**2003**	**2004**	**2005**	**2003**	**2004**	**2005**
Italy	140	139		3.2	3.7		450	513	
France	81	60		1.8	2.5		149	152	
EU-15	251	216		2.5	3.2		617	682	
10 new EU members	49	46		1.5	2.1		76	96	
EU-25	**300**	**261**	**283**	**2.3**	**3.0**	**3.1**	**693**	**777**	**888**

Table 2: European production of soybeans. Situation before and after the Europe expansion.
Sources: Oil world and PROLEA

The surface dedicated to the production of soybeans in the EU was in 2004 about 260 000 ha. More recent figures indicate an increase of 14% in the production to 888 000 tons. Italy is the main producer in Europe (66%), followed by France (20%).

The EU consumes more soy than its own production. The EU is the biggest importer of soybeans (14 Mt) and soy meal (20 Mt) (Source USDA). The main supplier countries are Brazil (9 Mt of soybeans and 9.1 Mt of soy meal), Argentina (10.1 Mt of soy meal) and USA (3.5 Mt of soybeans) (Source ICTS). Brazil and USA were selected for the human consumption soybeans as their products are not genetically modified. GM products from Argentina are utilized exclusively for animal feed. The European imports from Brazil are increasing recently due to their lower price associated to a non-GM product.

2. SOYBEAN OIL

With the soybeans imported from Brazil and USA, the European Union produces soy meal for its animal feed and soybean oil for human consumption (2.56 Mt). No importation of soybean oil is required as the European consumption is largely satisfied (2 Mt). The generated surplus (560 thousand tons) is then exported essentially to African countries (Table 3).

	Soybean oil EU exports (tons)
Angola	29 459
Senegal	9 295
Cameroon	8 609
Cape Verde	7 331
Suriname	5 402
Ghana	4 409
Fiji	3 960
Sudan	3 063
The Gambia	2 678
Guinea	2 444

Table 3: Importer countries of European soybean oil. Source: European Commission 2004.

The industrial non-food use of vegetable oils in Europe has increased in the last five years (Table 4). The recent oil crises have maintained a high price of crude oil and new alternatives for it have been developed, in particular the biodiesel and other bioproducts derived from different vegetable oils (see later Table 6).

	2002/03	**2003/04**	**2004/05**	**2005/06**	**2006/07 forecast**
Rapeseed Oil	1 247	1 783	2 598	3 600	4 430
Palm Oil	500	671	1 035	1 365	1 720
Soybean Oil	**280**	**335**	**400**	**1 175**	**1 375**
Sunflower Oil	83	82	95	95	100
Others	387	405	409	420	405
TOTAL	2 497	3 276	4 537	6 655	8 030

Table 4. Vegetable oils utilized in Europe for industrial uses. Figures are in thousand tons. Source: USDA.

Table 4 shows a clear progression of the soybean oil industrial use in Europe (+391% in 5 years). However, it is clear that rapeseed oil remains the most used in Europe and seems to keep this evolution. The European biofuels forecast production in 2010 is 2.5 Mt of biodiesel versus 1.4 Mt of bioethanol (Source: EU Commission).

Even if some figures are not consistent, the USDA/FAS provides in a 2006 report, a clear situation of the non-food uses of soybean oil versus the alimentary use (Table 5).

	2004/05	**2005/06**	**2006/07**
Crush	14 095	13 700	13 550
Extraction Rate	17.9 %	17.6%	17.6%
Beginning Stocks	215	230	210
Production	2 523	2 415	2 380
Extra EU-25 imports	163	350	450
TOTAL SUPPLY	2 901	2 995	3 040
Extra EU-25 exports	514	415	400
Industrial	400	600	775
Food Use	1 636	1 629	1 542
Feed, Seed, Waste	121	121	123
TOTAL USE	2 157	2 350	2 440
Ending Stocks	230	230	200
TOTAL DISTRIBUTION	2 901	2 995	3 040

Table 5. Balance of soybean oil production and consumption (by utilization). Figures are in thousand tons. Source: USDA/FAS.

The main uses of the industrial soybean oil in Europe are presented in Table 6 and Table 7.

Applications	Examples	Vegetable base
Lubricants and Hydraulic fluids	outdoor : chainsaw, agricultural engines	rape, oleic sunflower
	concrete form removal	rape
	fluids for oil drilling	rape
	metal work	rape esters
	two-stroke engines	oleic sunflower
Solvents	asphalt flux	sunflower esters
	phytosanitary additives	rape esters
	industrial degreasing, removal of paint	rape esters
Coatings and inks	varnish and paints	linseed, **soy**, sunflower, rape and castor
	inks	**soy and soy esters**, sunflower and rape
	wood protection	linseed
	linoleum	linseed
	polyurethane rigid foams	castor
Surfactants	cosmetics (creams, lipsticks…)	rape derivatives (including erucic), castor, glycerin
	soaps	linseed
	additives for machining	rape derivatives (including erucic),
Plastics	plasticizers and stabilizers	erucic rape derivatives and **soy**

Table 6. Main uses of the vegetable oils in Europe. Sources: PROLEA and EU Parliament.

	Austria	Belgium	Cyprus	Czech Rep.	Denmark	Estonia	Finland	France	Germany	Greece	Hungary	Irland	Italy	Latvia	Lithuania	Luxembourg	Malta	Netherlands	Poland	Portugal	Slovakia	Slovenia	Spain	Sweden	UK
Camelina	🟩	🟩			🟩			🟩	🟩				🟩					🟩					🟩		🟩
Castor								🟩																	
Cotton										🟩													🟩		
Crambe													R												🟩
Linseed	🟩	🟩		🟩	D	🟩	🟩	🟩	🟩		🟩		🟩	🟩	🟩			🟩						D	🟩
Palm								🟩																	
Rapeseed	🟩	🟩			🟩		🟩	🟩	🟩		🟩		🟩		🟩			🟩	🟩				🟩	🟩	🟩
Soya	🟥							🟥					🟥										🟥		
Sunflower	🟩							🟩	🟩	🟩	P		🟩							🟩			🟩		
	Aus	**Bel**	**Cyp**	**Cze**	**Den**	**Est**	**Fin**	**Fra**	**Ger**	**Gre**	**Hun**	**Irl**	**Ita**	**Lat**	**Lit**	**Lux**	**Mal**	**NL**	**Pol**	**Por**	**Slk**	**Slv**	**Spa**	**Swe**	**UK**
Surfactants	🟦	🟦		🟦	🟦		🟦	🟦	🟦	🟦														🟦	🟦
Lubricants	🟦	🟦		🟦	D		🟦	🟦	🟦	P	R		D		🟦			🟦						🟦	🟦
Paints	P	🟦		🟦	🟦	🟦	🟦	🟦	🟦			P												🟦	🟦
Solvents		RD						🟦	🟦									🟦							D
Polymers								🟦	🟦																
Linoleum		🟦		🟦					🟦																🟦

Table 7. Main uses of the vegetable oils in Europe. Classification by country, by oleaginous and by application. Full cell: Current activity; D:Development; R:Research. Source: European Parliament.

In conclusion, soybean oil is a niche market in Europe. The non-food applications are essentially in the coating, inks (as solvent) and plastic fields.

In the oral presentation, it will be discussed the perspectives of growing activities in Europe of soybean oil industrial products.

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USE OF SOYBEAN OIL IN INDUSTRIAL LUBRICANTS

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There has been a steady increase in the demand for environment friendly lubricants. Vegetable oils are promising candidates as base fluid for eco-friendly lubricants because of their excellent lubricity, biodegradability and low evaporation loss. Their use, however, is restricted due to low thermo-oxidative stability and poor cold flow behavior. This paper presents a systematic approach to improve the oxidation and cold flow behavior of vegetable oil derivatives (chemical modification and additive technology). Soy oil based lubricants formulated using the above approach exhibit superior oxidative stability, improved low temperature properties such a pour points and better wear properties compared to some of the commercially available industrial oils. The above technology has been patented (U.S. Patent 6,583,302) and currently is being used in the hydraulic elevator fluid industry.

Key words: soybean, vegetable, oils, lubricants, biodegradability

POLYOLS AND POLYURETHANES FROM VEGETABLE OILS

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Abstract

Polyols from vegetable oils have specific structure depending on the nature of oil and the way of preparation. The main difference arises from the wide distribution of functionality, which in oil-based polyols is wider than in petrochemical polyols. Structural heterogeneity of oil-based polyols is also much wider. This heterogeneity affects properties of polyurethanes, particularly at low hydroxyl numbers.

Introduction

Polyurethanes from vegetable oil polyols are a class of materials from renewable resources with some very promising competitive advantages, such as, hydrophobicity, higher thermo-oxidative stability and favorable price. Vegetable oil polyurethanes are attractive because they offer some properties related to the specific structure of oils, as well as concerns about the environment and sustainability. The most popular oils for such applications due to their availability and economics are: soybean oil in the US and South America, rapeseed oil in Europe, and palm oil in Asia. Vegetable oils are abundant and relatively inexpensive raw materials offering some economic advantages. However, they are heterogeneous materials with a wide distribution of triglyceride structures differing in the content of double bonds. Such heterogeneity is reflected in properties of resulting polyols, their reactivity (processing characteristics) and properties of oil-based polyurethanes. Soybean oil, which will be discussed in this presentation, is a semi-drying oil with relatively high unsaturation. It is a mixture of triglycerides of predominantly five fatty acids, three unsaturated - oleic (O), linoleic (L), linolenic (Ln) and two saturated fatty acids (S) - palmitic and stearic. A schematic representation of soybean oil structure is given in Figure 1, but individual molecule structures would vary.

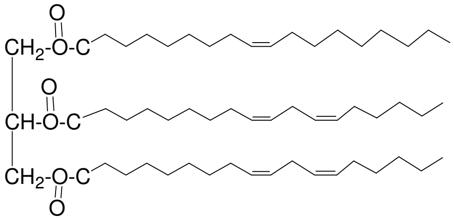

Figure 1. Schematic representation of soybean oil structure

On average, soybean oil has typically about 4.5 double bonds per triglyceride, but individual triglycerides have a distribution of double bonds, theoretically from zero to nine. Figure 2 displays the distribution of functionalities in a soybean oil calculated from literature data.[1] If all double bonds were converted to hydroxyl, the polyol would be a powerful crosslinker and as such suitable for rigid polyurethane applications. The applications of oil-based polyols would depend on the properties of networks from such mixtures.

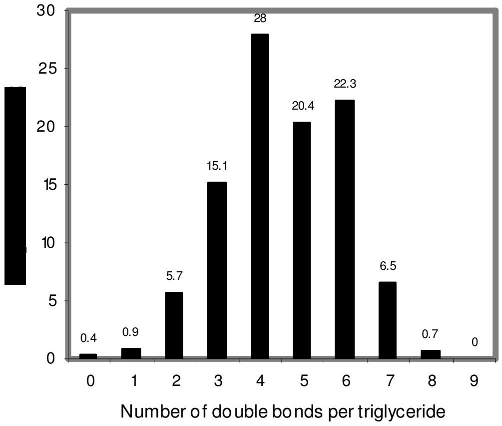

Figure 2. Distribution of triglycerides with different content of double bonds

The structure of polyols depends on the synthesis method. There are several routes to make polyols which are of potential interest for commercialization: epoxidation with ring opening, hydroformylation, ozonolysis, transesterification and direct oxidation. Direct oxidation was the first method used for commercial products giving the lowest price polyols. However, due to statistical nature of the process the products may have a range of oxidation products such as aldehyde, hydroxyls, acids, ketones and chain scission. These products were characterized with dark color, strong smell and low functionality in addition to the presence of a considerable amount of non-reactive species. Epoxidation route requires preparation of epoxidized soybean oil (ESBO) and ring opening by different reagents such as inorganic acids, organic acids, alcohols, water and hydrogenation, Figure 3.[2] ESBO has been a commercial product for a long time, mainly used as a plasticizer for PVC. The polyols prepared this way are usually clear liquids or waxes with well controlled functionality and give polyurethanes with excellent properties, which depend on the hydroxyl number. However, they have secondary hydroxyl groups and are generally less reactive.

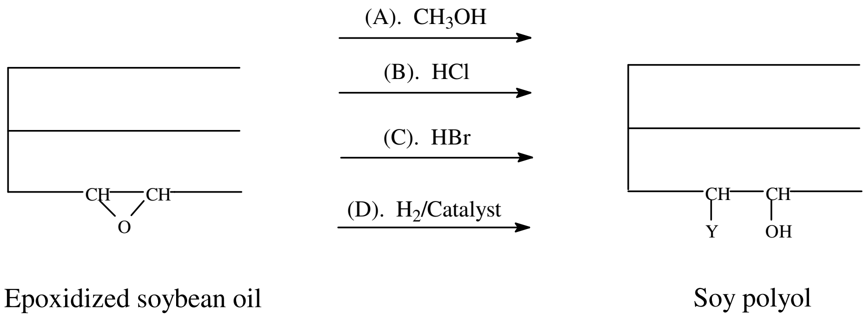

Figure 3. Preparation of polyols from epoxidized soybean oil

Polyols prepared by hydroformylation have primary OH groups and are thus very reactive. The process gives polyols with well defined structure and the highest functionality. The advantage of this process is that all the components in the reaction end in the product and as such the process is environmentally friendly. The catalysts used for the process may be very expensive and complete recovery is necessary to be economical.

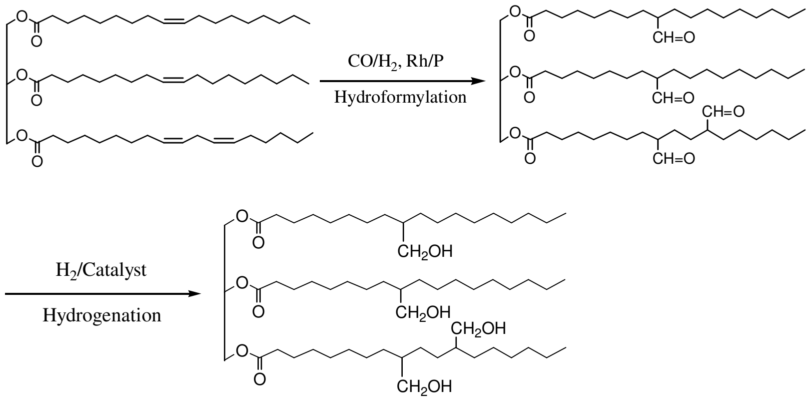

Figure 4. Hydroformylation method for preparation of soy-oil based polyols

Polyols with primary OH groups and more regular structure are obtained by ozonolysis of SBO. Because of structural regularity these polyols tend to crystallize giving waxes at room temperature.[3] However, they are excellent materials for coatings, sealants, adhesives, and as modifiers for urethane foams. Crystallization may be avoided at the expense of increasing structural heterogeneity.[4] A major effect on the economics of the ozonolysis is the cost of electricity necessary to generate ozon. Otherwise, ozonolysis is an extremely efficient process.

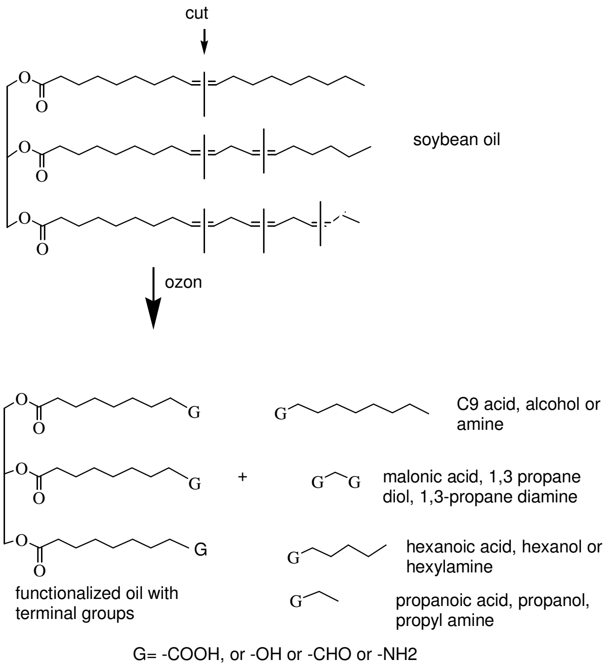

Figure 5. Ozonolysis products from SBO

Transesterification is a process that may be used to reduce triglycerides to diglycerides, monoglycerides, and fatty acids by reacting with polyvalent alcohols and to free some hydroxyl groups from glycerin. It has been applied to modify some polyols prepared by other routes. Transesterification is used to obtain fatty acids and their derivatives, which can be used for further chemistries. Fatty acid–based polyols have a lower viscosity but also lower functionality than triglyceride polyols; but if esters bonds are avoided, they may claim higher hydrolytic stability. Figure 6 gives comparative properties of polyurethanes prepared by the epoxidation route (Polyol 173 and 200 and hydrogenated ESBO- HESBO), hydroformylation (HF), fatty acid polyol obtained by glycolysis of polyol 173, ozonolysis polyols. Vegetable oil polyols cannot be used as the sole polyols in flexible foams because of their heterogeneity and low molecular weight. One way to overcome this difficulty is to prepare hybrid polyols by propoxylation of some of the polyols listed above.[5,6]

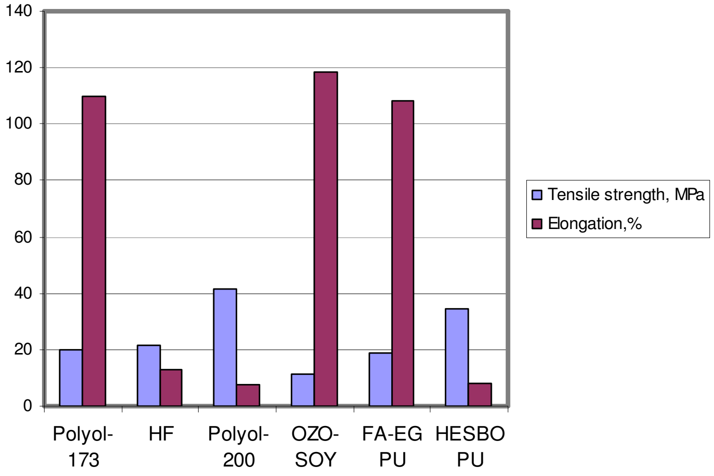

Figure 6. Comparative properties of polyurethanes prepared different methods

Conclusion

Useful vegetable oil polyols can be prepared by different methods and serve different application fields. Polyurethanes obtained from polyols by epoxidation route have the highest rigidity and strength. Hydroformylation gives polyols with highest reactivity and somewhat “softer” polyurethanes. Ozonolysis gives the highest regularity of the structure and excellent properties in the absence of dangling chains. Fatty acid polyols have the lowest viscosity and a high OH number but give about the same properties of polyurethanes as the triglyceride polyol that they are derived from.

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Key words: polyol, polyurethanes, vegetable oil

SOY PROTEIN POLYMERS FOR ADHESIVES

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Key Words: Soybean, Protein Polymers, Adhesives

Introduction

About 20 billion lb of adhesives are used annually in the U.S. in the production of plywood, particleboard, labeling, packaging, and sizing, among other things. The various forms of wood adhesives represent an extremely large and diverse market, probably the largest in the world today [1]. Soy-based adhesives were first developed in 1923 when a patent was granted for a soy meal-based glue [2]. However, those soy protein adhesives have low gluing strength and little water resistance. Adhesives produced from petroleum-based chemicals have overcome those disadvantages, but many concerns have surfaced about air quality and environment pollution, and even toxicity during product manufacturing, distribution, and use. Among these adhesives, about 8 billion lb are formaldehyde-based adhesives annually used by wood-based product industries. The greatly expanding markets for adhesives, the threat of limited world oil reserves, and the increasing concern over environmental pollution has forced industry to seek new adhesives from biobased polymers. Protein modification is designed to improve functional properties by altering protein molecular structure or conformation, through physical, chemical, or enzymatic agents, at the secondary, tertiary, and quaternary levels. Soy protein has potential for the production of adhesives with high gluing strength and improved water resistance [3,4,5].

Proteins are complex macromolecules that contain a number of chemically linked amino acid monomers, containing primary, secondary, tertiary, and quaternary structures. Proteins can be modified through physical, chemical, and enzymatic methods, all resulting in structural or conformational changes from the native structure without altering the amino acid sequence. A modification that changes secondary, tertiary, or quaternary structure of a protein molecule is referred to as denaturation [7]. The compact protein structure unfolds or cross-links during denaturation, which is accompanied by the breaking and re-forming of the intermolecular and intramolecular interactions [8]. Protein modification could also turn some hydrophobic amino acids, which are buried inside, outwards to increase water resistance.

Protein Unfolding

A modification that changes secondary, tertiary, or quaternary structure of a protein molecule is referred to as denaturation [8]. The compact protein structure unfolds or cross-links during denaturation, which is accompanied by the breaking and re-forming of the intermolecular and intramolecular interactions [15]. Protein modification can also turn some hydrophobic amino acids, which are buried inside, outwards to improve water resistance. Protein denaturation can be induced by pH (alkali or acid), detergents, chemicals with reactive groups, such as amino, hydroxyl, carboxyl, iasocyanate, etc., as well as by heat treatment. The degree of change is influenced not only by modifier chemical structure, but also by chemical concentration and modification procedures.

Adhesive Properties

Hydrophobic interactions induced by soy proteins modification with various SDS concentrations are proved to have different adhesive properties [4]. With pH about 7.0, proteins modified with 0.5 and 1% SDS gave the highest gluing strength (Table 1). Soy protein modified with sodium dodecylbenzene sulfonate (SDBS), another anionic detergent, in the similar concentration range as SDS, presented similar gluing property reported by Huang and Sun [4]. The soy proteins modified with 1% SDS also had higher water resistance, showing no change in gluing strength after exposing to high relative humidity [4]. Wood specimens glued with the 1% SDS modified protein adhesive had about 10% reduction in shear strength after three water-soaking cycles (Table 1).

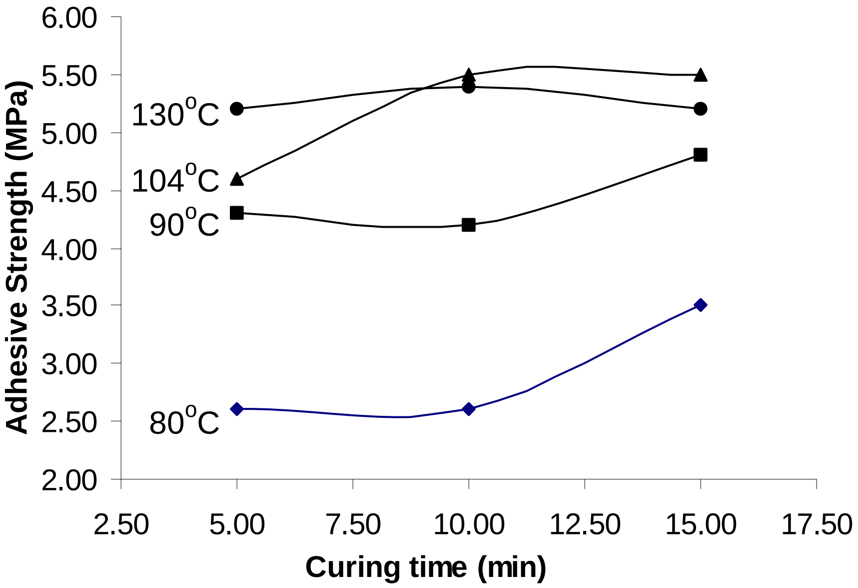
Table 1. Adhesive strength (MPa) of unfolded soy proteins with sodium dodecyl sulfate (SDS) on cherry wood samples. The soaked strength is referred to the strength after three-cycle of 48 hr water soaking test.

SDS concentration (%)	Dry strength (MPa)	Soaked strength (MPa)	Ref
0	4.1	0	[4]
0.5	5.4	3.3	[4]
1.0	5.5	4.9	[4]
3.0	3.8	3.2	[4]

Effects of Curing Temperature and Pressure On Adhesive Strength

Proteins are temperature and pressure sensitive polymers. Curing temperature, pressure, and time, are important influences on the final protein structure re-conformation, mutual diffusion at the interface, and consequently, the adhesion strength. The structure change induced by modification requires different curing conditions. Temperature and time are important factors affecting curing strength [32]. One experiment reported by Sun and Bian [34] demonstrates the relations among adhesive curing strength-curing temperature-curing time (Figure 1). Longer curing time is needed at lower curing temperature. For example, with a fixed press pressure (20kg/cm^2), about 5 min is needed to reach the highest gluing strength at 130ºC, but it takes about 15 min to obtain a similar curing strength at 90ºC.

Fig. 1. Effects of curing temperature and time on adhesive strength of soy protein modified with 3 M urea pm walnut wood samples. Data source is from reference [34].



In another experiment done by Zhong et al. [33], similar results are also obtained that gluing strength of fiber cardboard with soy protein adhesive increased significantly as curing temperature increased up to 100 °C.

Soy Protein Latex Like Adhesives

Multi billion lb latex based adhesives are used annually in the US. They include foundry adhesives, wood adhesives, school children glues, labeling adhesives, paper box packaging adhesives, and envelope adhesives. Most latex based adhesives are synthetic chemicals and contain vinyl acetate or acetaldehyde, which are especially restricted for food and pharmaceutical related products packaging.

Unfolded protein in low moisture content also enables protein molecules entangled each other forming continuous complex that has strong tack adhesion properties, which is so called “latex” like adhesive in this section. This adhesive is fluid like with solid content ranging from 20 to 70% (Fig. 2). The latex like adhesive has long shelf life up to eight month at room condition and no protein-water phase separation in storage and application. This adhesive in various formulas can be used as children glue and color paint, wood veneer adhesive, fiber composite resin, foundry adhesives, and packaging and labeling adhesives.

Fig. 2. Soy protein based latex like adhesive sample with 37% moisture content

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SOYBEAN MEAL: A LOW-COST PRODUCT WITH POTENTIAL HIGH-VALUE APPLICATION

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Key Words: Soybean meal, soybean proteins, plywood glue, biobased product, nonfeed use

Introduction

Soybean meal is the predominant co-product from the processing of soybean, accounting for 80% of material output. It is generally considered the most valuable end product because it contributes 50-75% of the processing value (Ash et al., 2006). Soybean meal production in the United States was 41.6 million tons in 2006, with 33.2 million tons consumed domestically and 8.1 million tons exported (Oil Crops Outlook, 2007). Soybean meal contains 48% crude protein (CP) and its primary use is as protein supplier in livestock feed, which uses up to 98% of US soybean meal consumption. The remainder is used for human foods (e.g., baked goods, meat substitutes, infant formulas, and beverages). Soybean meal is the most inexpensive among the various soy protein products, selling for about $0.17/kg (Oil Crops Outlook, 2007) compared with $0.48/kg for flour (55% CP), $2.05/kg for concentrate (65-70% CP), and $2.70 for isolate (at least 90% CP) (prices supplied by commercial manufacturers). Because of its abundant quantity, ready availability, and low cost, soybean meal has been and continues to be an attractive starting material for developing bio-based products.

From the 1930s until after World War II, soybean meal figured prominently in such products as paper laminate glue, wood adhesives, textiles, and molded plastics (Bowden, 1937; Brother, 1938; Finlay, 2004). However, the emergence of cheaper, synthetic alternatives relegated soybean meal to feed use. In recent years, there has been renewed interest in soybean meal for non-feed uses, which was brought about by the significant momentum gained by the commercial development of the biodiesel industry (Ash et al., 2006). Although soybean oil is the commodity that is directly affected in biodiesel production, it is expected that meal production will consequently expand as well (Raneses, et al., 1999).

At the U.S. Department of Agriculture's National Center for Agricultural Utilization Research, our research group has been developing new uses for the proteinaceous co-products from soybean and cereal processing. One of our success stories is soy flour-based foamed plywood glue that is now being used commercially by one of the largest plywood manufacturers in the United States

(Hojilla-Evangelista, 2002). We are now focusing on soybean meal as an alternative protein extender in plywood adhesives.

Evaluating Soybean Meal in Plywood Glues

During our earlier research on foamed plywood adhesives, we evaluated several commercial soybean protein sources, such as meal, flour, concentrate and isolate (Hojilla-Evangelista and Dunn, 2001). We found that soybean meal had poor solubility and foaming properties, and was thus not suitable for foamed plywood glues. However, we observed from SDS-PAGE results that the major protein sub-units were still present in soybean meal and showed a pattern that was similar to those of undenatured water-extractable soybean proteins (Fig. 1, lane 5). This finding suggested that it may be possible to make the soybean meal protein more reactive by physical (e.g. grinding) and/or chemical means. The highly alkaline pH of plywood glues (as high as pH 12) could be an ideal environment for modifying the meal protein through unfolding of the structure and increasing the available reactive sites.

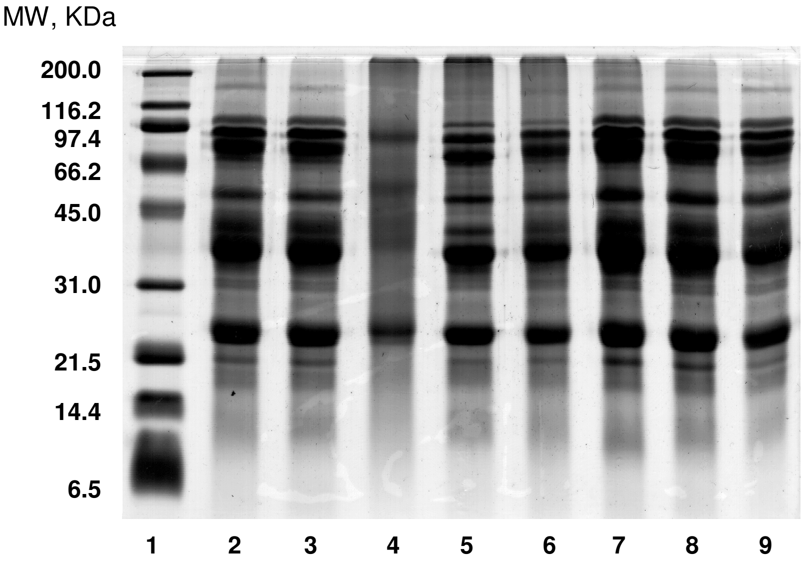

Fig. 1. SDS-PAGE band patterns for commercial soy flours and soybean meal: (1) molecular weight standards, (2) Soyafluff flour, (3) Nutrisoy 7B flour, (4) ProCote PX 245, (5) ADM soybean meal, (6) Centex 4030, (7) Honeysoy 70 flour, (8) Honeysoy 90 flour, and (9) soy flour from Iowa State University-Center for Crops Utilization Research.

The effect of grinding on protein solubility was first determined. Solubility is an important property because it affects the dispersion of the protein during the initial mixing step in glue manufacture. Soybean meal (Archer Daniels Midland, Decatur, IL) was ground in a coffee mill for 2 min to obtain 40-mesh particle size. The amounts of soluble protein were determined at pH 7 and pH 10 (glue pH) according to methods described by Hojilla-Evangelista and Dunn (2001) and compared with values from meal that was left as received from the manufacturer (i.e., granular, 10-mesh particle size). The amount of protein extracted from the meal at pH 7 and pH 10 increased after grinding to 40-mesh size (Table 1). This was not surprising because the larger surface area allowed for more contact with the aqueous solvent. SDS-PAGE also showed no difference in the band patterns or intensities of the soybean meal protein before and after mixing, which indicated that the grinding conditions had no detrimental effect.

Table 1. Effect of grinding on solubility of protein in soybean meal

Sample	Soluble Protein (%)	
	pH 7	pH 10
Soybean meal, as is	9.7 ± 2.8	28.9 ± 3.4
Soybean meal, ground to 40-mesh	14.4 ± 1.1	34.7 ± 1.5

Values are mean ± standard deviation for duplicate determinations.

We then selected plywood glue intended for sprayline application as the media for testing the performance of the soybean meal. This type of glue does not require any foaming capability and is more tolerant of non-protein constituents (e.g. oil) of the extender than glues for foam extrusion. Wheat flour (10% CP) is the protein extender currently used by industry in sprayline glues. The standard glue mix (30% mix resin solids) was made up of 13.6 g water, 6.1 g protein extender, 7.0 g filler, 69.8 g phenol-formaldehyde (PF) resin, and 3.0 g 50% NaOH. Ground soybean meal was substituted for wheat flour either on a quantity or protein content basis. After several trials, three soybean meal-based formulations (Table 2) were selected based on their desirable mixing properties and acceptable viscosities.

Table 2. Standard and soybean meal-based plywood glues for sprayline coater

Ingredients	Glue Mixes (100-g quantity)			
	A Standard Mix (10.5 % CP, db)	**B** Soybean Meal (51.5% CP, db)	**C** Soybean Meal (51.5% CP, db)	**D** Soybean Meal (51.5% CP, db)
Water, g	13.6	13.6	15.3	15.1
Protein extender, g	6.1	1.2	6.1	4.6
Filler, g	7.0	11.9	5.2	7.0
PF resin, g	69.8	69.8	69.8	69.8
50% NaOH	3.0	3.0	3.0	3.0

Glue **A** - Control glue with wheat flour extender

Glue **B** - Protein content-based replacement of extender

Glue **C** - Total extender replacement, 25% reduction of filler, increased water (by 1.75 g from filler reduction)

Glue **D** - Extender at 75% of original amount, increased water (by 1.52 g from extender reduction)

Glues were applied by a roll coater onto 12 in x 12 in (30.5 cm x 30.5 cm) Southern pine veneers. Three-ply wood panels were made by hot-pressing assembled veneers for 3 min at 325°F and 250 psi. Wet tensile strengths of plywood test specimens were determined by using a plywood testing machine (Globe Machine Manufacturing Co., Tacoma, WA). Glues were considered strong if their wet tensile strength values were at least 200 psi. Only the standard glue containing wheat flour extender had wet tensile strength that was greater than 200 psi, but the value was just marginally better than those obtained for the soybean meal glues (Table 2). We are presently making adjustments in the mixing protocol and formulations to improve the bonding strengths of the soybean meal plywood adhesives. However, our results already show that soybean meal has strong potential to be an alternative protein extender in plywood glues for sprayline coater.

Table 3. Wet tensile strengths of plywood bonded by standard or soybean meal-based glues

Glue Code	Protein Extender	Tensile Strength, psi
A	Wheat flour	213 ± 50
B	Soybean meal	186 ± 36
C	Soybean meal	188 ± 16
D	Soybean meal	178 ± 17

Values are mean ± standard deviation for at least 16 test specimens per plywood panel.

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Glycerol
Production and Utilization

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Filtration & Membrane World LLC

Properties

Glycerol, glycerin, 1, 2, 3-propanetriol

- Discovered in 1779 by Scheele
- Sources include
  - Natural: fats and oils
  - Synthetic: petrochemical

Glycerol Properties

– Melting point	17.8 °C
– Boiling point (1 atm)	290 °C
– Density (25 °C)	1.262 g/ml
– Flashpoint (open cup)	176 °C
– Solubility	water, ethanol
– Toxicity	20 mL/kg (oral)

Highly Functional

- Glycerol contains one secondary and two primary alcohol groups per molecule
- Reacts with organic and inorganic acids to form aldehydes, esters, ethers and many derivatives
- The presence of multiple alcohol groups facilitates the formation of polymers and coatings
  - Polyesters, polyethers
  - Alkyd resins

Water Soluble

- Glycerol is separated and purified from aqueous solutions by physical processes
- Acts as both a solvent and reactant
  - Syntheses may be performed ‘solventless’
  - Reaction products are easily recovered
- Useful in the development of green processing technologies

Non-toxic

- Biocompatible
  - Synthesized by plants and animals
  - Glycerol is metabolized to pyruvate
- Safe in topical formulations
  - Ingredient in personal care products
- Approved for pharmaceutical applications

Environmentally Significant

- Biodegradable co-polymers of glycerol and lactic acid
  - Polyesters, polycarbonates
- Development of glycerol ethers as oxygenated fuel additives to improve combustion

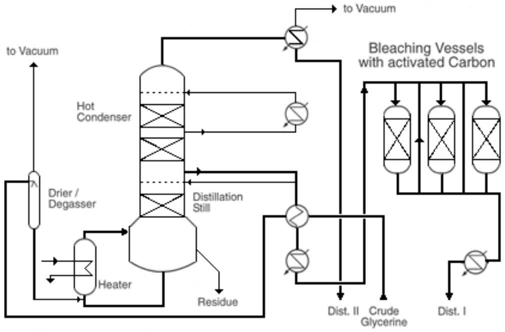
Production

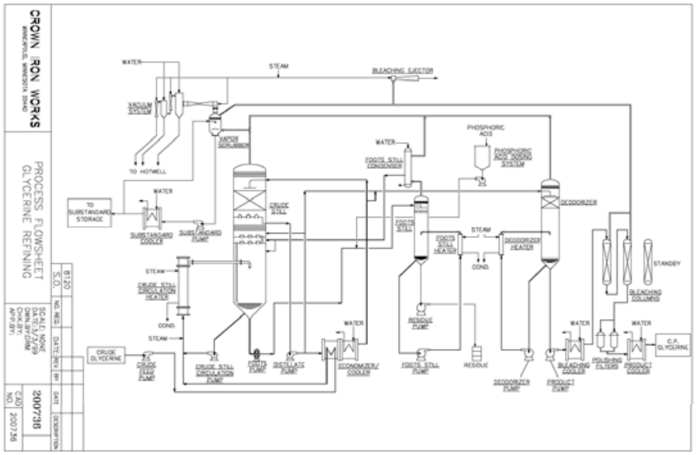
Glycerol Production

- Fats and oils processing
  - – Saponification
  - – Hydrolysis
  - – Transesterification (Biodiesel)
- Product quality
  - – Crude: 80 – 90% glycerol
  - – Refined: 99.7%, USP (0.35 - 0.75 $/lb)

Glycerol Production

- **Glycerin Refining;**
- **The crude sweet water is purified, evaporated and gently distilled in a vacuum with the admission of live steam. The distillate is withdrawn at near boiling point and free from low volatile components before being bleached.**





Biodiesel Process

- Reactants
  - Vegetable oil (FFA value < 1%)
  - Methanol (ethanol or other alcohol)
  - Catalyst, e. g., KOH, sodium methoxide
- Products
  - Methyl soyate
  - Crude glycerol
    - Separator stream ~40% glycerol
    - Evaporator stream ~80% glycerol

Material Balance

- A molecule of fat or oil is hydrolyzed to produce glycerol and three fatty acids

- Production of biodiesel generates glycerol in the corresponding mole ratio

- Increasing biodiesel production will result in additional glycerol in the market

Biodiesel Specifications

Property	**ASTM**	**Limits**	**Units**
Flash Point	D93	130 min.	°C
Water & Sediment	D2709	0.050 max.	% vol.
Kinematic Viscosity	D445	1.9 - 6.0	mm2/sec.
Sulfated Ash	D874	0.020 max.	% mass
Sulfur	D5453	0.05 max.	% mass
Corrosion	D130	No. 3 max.	
Cetane	D613	47 min.	
Cloud Point	D2500	Report	°C
Carbon Residue	D4530	0.050 max.	% mass
Acid Number	D664	0.80 max.	mg KOH/gm
Free Glycerin	D6584	0.020 max.	% mass
Total Glycerin	D6584	0.240 max.	% mass
P Content	D 4951	0.001 max.	% mass

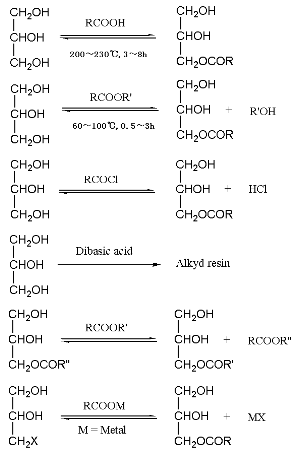
Derivatives

Specialty Chemicals

- C3 building block for complex structures
- Easily modified through functional groups
- Acceptable synthon for green chemistry
- Water soluble, nontoxic, nonflammable

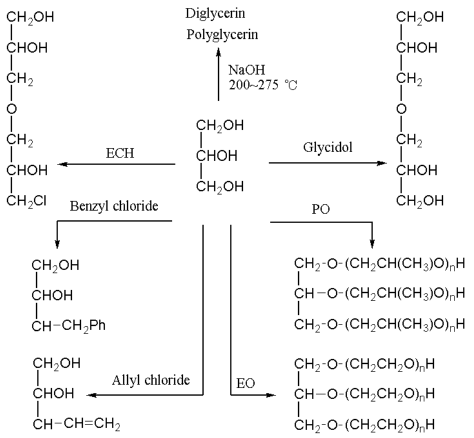
Glycerol Properties

- Esterification



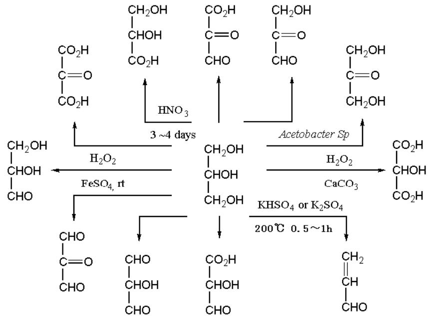
Glycerol Properties

- Etherification



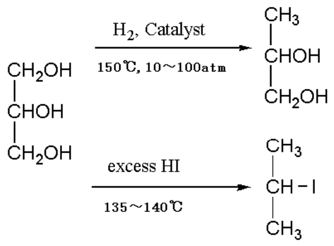
Glycerol Properties

- Oxidation



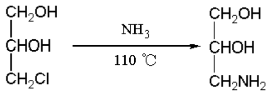
Glycerol Properties

- Reduction



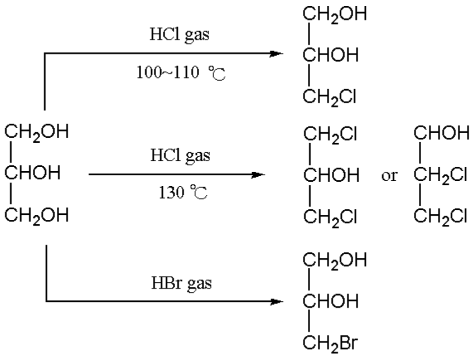
Glycerol Properties

- Amination



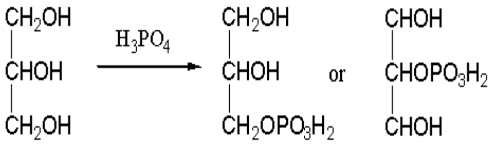
Glycerol Properties

- Halogenation



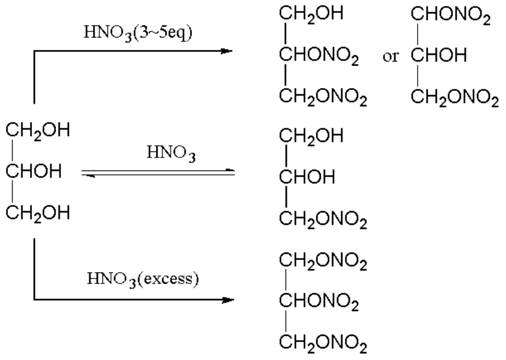
Glycerol Properties

- Phosphorylation



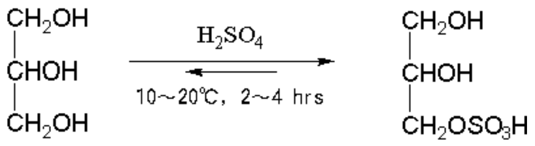
Glycerol Properties

- Nitration



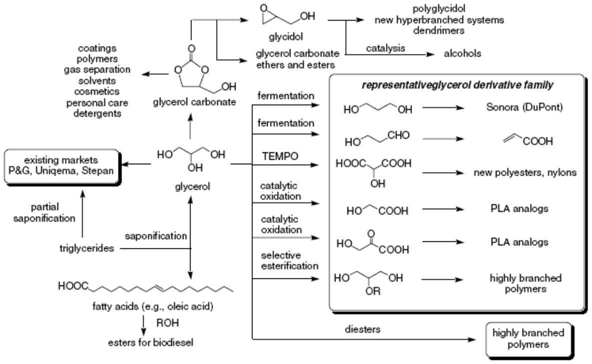
Glycerol Properties

- Sulfaction



Glycerol Properties

- **Families of Possible Glycerol Reactions (source: Biomass oil analysis: research needs and recommendations)**



Utilization

Glycerol Applications (cont'd)

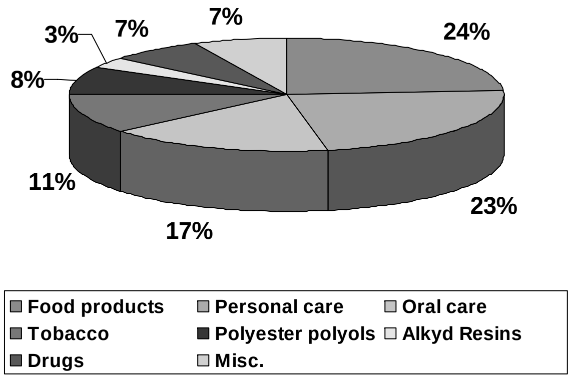
- Solvent, humectant
- Excipient
- Fermentation substrate
- Emollient
- Sweetener
- Plasticizer
- Antifreeze
- Wood preservative

Glycerol Applications

- Adhesives
- Cements
- Ceramics
- Cleansers
- Hydraulic fluids
- Lubricants
- Polishes

Glycerol Utilization by Industry

- Cosmetics
- Explosives
- Food
- Pharmaceutical
- Polymer
- Printing



Glycerol Applications (cont’d)

- **Drugs;**
- Used in medical and pharmaceutical preparations, mainly as a means of improving smoothness, providing lubrication and as a humectant. Also may be used to lower intracranial and intraocular pressures.
- Laxative suppositories, cough syrups, elixirs and expectorants.

Glycerol Applications (cont’d)

- **Personal care;**

- Serves as an emollient, humectant, solvent and lubricant in personal care products
- Competes with sorbitol although glycerin has better taste and higher solubility.
- Toothpaste, mouthwashes, skin care products, hair care products and soaps
- Glycerin is a component of glycerin soap, which is made from denatured alcohol, glycerin, sodium castorate (from castor), sodium cocoate, sodium tallowate, sucrose, water and parfum (fragrance). Sometimes one adds sodium laureth sulfate. This kind of soap is used by people with sensitive, easily irritated skin because it prevents skin dryness with its moisturizing properties.

Glycerol Applications (cont’d)

- **Foods and beverages;**

- Serves as humectant, solvent and sweetener, may help preserve foods.
- Solvent for flavors (such as vanilla) and food coloring.
- Humectant and softening agent in candy, cakes and casings for meats and cheeses.
- Manufacture of mono- and di-glycerides for use as emulsifiers
- Used in manufacture of polyglycerol esters going into shortenings and margarine.
- Used as filler in low-fat food products (i.e., cookies).
- Glycerin has approximately 27 food calories per teaspoon and is 60% as sweet as table sugar. Although it has about the same food energy as table sugar, it does not raise blood sugar levels, nor does it feed the bacteria that form plaques and cause dental cavities. Glycerin should not be consumed undiluted, as unhydrated glycerin will draw water from tissues, causing blistering in the mouth and gastric distress. As food additive, glycerin (glycerol) is also known as E number E422.

Glycerol Applications (cont’d)

- **Polyether polyols;**

- One of the major raw materials for the manufacture of polyols for flexible foams, and to a lesser extent rigid polyurethane foams
- Glycerin is the initiator to which propylene oxide/ethylene oxide is added

Glycerol Applications (cont’d)

- **Alkyd resins (plastics) and cellophane;**

- Used in surface coatings and paints
- Used as a softener and plasticizer to impart flexibility, pliability and toughness
- Uses include meat casings, collagen casings (medical applications) and nonmeat packaging
- Plasticizer in cellophane.

Glycerol Applications (cont’d)

- **Absolute alcohol;**

- There is an absolute alcohol production process by dehydration using glycerin; Mariller-Granger Processes (Alcoholic vapors passing through pure glycerine yield 99.2 alcohol directly)

Glycerol Applications (cont’d)

- **Other applications;**

- Manufacture of paper as a plasticizer, Nitroglycerin, humectant and lubricant
- Humectant for pet foods to retain moisture and enhance palatability
- Used in lubricating, sizing and softening of yarn and fabric
- Used in de-/anti-icing fluids, as in vitrification of blood cells for storage in liquid nitrogen
- Patent applications have been filed for detergent softeners and surfactants based on glycerin (i.e., alkyl glyceryl ethers) instead of quaternary ammonium compounds.

Glycerol Applications (cont’d)

- Can be added to solutions of water and soap to increase that solution's ability to generate soap bubbles that will last a long time.

- Use as antifreeze in cryogenic process.

- Used in fog machine fluids

- Used in hookah tobacco mixtures (called "ma'assel" or "shisha" tobacco), often along with molasses and/or honey.

Strategies to Increase Glycerol Utilization

- Expand existing markets
- Develop new markets
  - Identify new applications
  - Develop new products

Glycerine

PRODUCER	CAPACITY*
Cognis, Cincinnati, Ohio	65
Colgate-Palmolive, Jeffersonville, Ind.	20
Crompton, Mapleton, Ill.	20
Crompton, Memphis, Tenn.	30
Dial, Montgomery, Ill.	30
Dow, Freeport, Tex.	140
Lever, Hammond, Ind.	25
Lonza, Painesville, Ohio	20
Marietta American, Olive Branch, Miss.	2
Procter & Gamble, Ivorydale, Ohio	150
Starchem, Fostoria, Tex.	20
Uniqema, Chicago, Ill.	35
Total	557

*Millions of pounds per year of refined glycerine.

STRENGTH

The market growth 3.5 percent annually (aging "baby boom" generation consumes more skin care cream).

The strong growth in sun screen lotions.

Good solubility and taste give glycerine an edge on sorbitol in toothpastes and mouth washes (1.5 percent annual growth)

The best performing sector, is food. (Continuing trend towards lowering the fat content in foods, particularly baked goods). (4 percent annual growth)

WEAKNESS

There is a significant increase of crude glycerine in biodiesel-related generation

Glycerine's use in polyether polyols and alkyd resins is shrinking at 1 percent and 1.5 percent annually.

DEMAND

1999: 427 million pounds;
2000: 453 million pounds;
2004: 494 million pounds,

GROWTH
Historical (1995 - 2000): 1.9 percent per year;
Future: 2.2 percent per year through 2004.

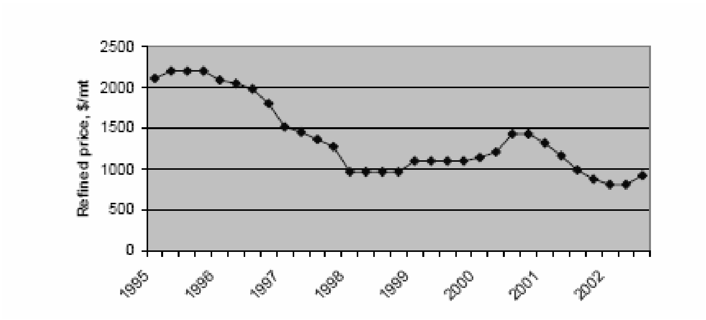
PRICE

Historical (1995 - 2000): High, $1.08 per pound, list, refd., USP, CP, non-kosher, 99.7 percent, tanks, dlvd.;

low, $0.60, same basis. Current: $0.60, same basis.

Strategies to Increase Glycerol Utilization

- Recent Glycerol Price History; Small increase in fatty acid consumption for fuels and products can increase world glycerin production significantly. The Expansion of biodiesel in Europe in recent years has had a major impact on glycerol prices.



Related Legislation

- Goals set by the Biomass Research and Development Act of 2000 and EO 13134
  - Develop and promote the use of bio-based products and bio-energy
  - Triple the use of biobased products and bioenergy by 2010

Glycerol: Replacement for Petrochemical Feedstocks

- Renewable
- Domestically produced
- Easily derivatized
- Nontoxic
- Nonflammable
- Available in high purity

Areas for Product Development

- Biomedical applications
- Coatings and polymers
- Specialty and fine chemicals

New Products and Applications

- Conversion of glycerol into substrates for the synthesis of specialty chemicals
  - Oxidation to aldehydes and acids
  - Condensation to acetals and ketals
- Development of new glycerol-based surfactants
  - Nonionics
  - Amino-esters
- Formation of glycerol/oil microemulsions for polymerization reactions
  - Biodegradable coatings
  - Biocompatible IPN

Conclusions

- Proven ingredient for cosmetic and personal care formulations
- Approved for human pharmaceutical and veterinary applications
- Plasticizer for polymers and coatings
- Anti-freeze, corrosion inhibitor
- Fermentation substrate (lactic, propionic, succinic acids)

Summary

- Glycerol is a renewable material available in high purity from biodiesel production
- Glycerol is nontoxic, biodegradable, and biocompatible
- Glycerol is a versatile substrate that may be converted into numerous biobased products

Polimerização Oxidativa de Tintas Alquídicas

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Palavras chave: oleoquímica, óleos vegetais, resinas alquídicas, catalisadores metálicos, tintas.

Na indústria de tintas a utilização de óleos vegetais é muito expressiva, pois vários materiais resínicos formadores de filmes sólidos são constituídos a base dos mais diversos óleos, tais como soja, DCO (óleo de mamona desidratado), linhaça, tungue, entre outros. Entre estes sistemas destacam-se os as resinas alquídicas, pois são aplicados como veículos em vários segmentos, como tintas decorativas e tintas industriais. Em 2006 foi consumido, no mercado nacional, um valor superior a 120 milhões de litros de resinas alquídicas.

O termo “resinas alquídicas” é aplicado a materiais poliméricos resinosos obtidos pela reação de poliálcoois e poliácidos. O próprio nome “alquídica” vem da palavra ALKID, derivada dos termos ingleses ALCOHOL e ACID. Este tipo de material polimérico é amplamente utilizado como veículo na indústria de tintas devido às suas propriedades, que permitem sua utilização numa variada gama de segmentos. Dentre as características das resinas alquídicas podemos citar: boa aderência sobre substratos, grande resistência a intempéries, riscos e abrasão e boa dureza e flexibilidade aliadas à baixo custo.

As resinas alquídicas são obtidas sinteticamente via reação de esterificação, entre poliácidos, ácidos graxos ou óleos vegetais e polióis. Dependendo do óleo vegetal empregado estas resinas podem ser consideradas, segundo à velocidade com que vão formar o filme após aplicação da tinta, como secativas (linhaça, tungue), semi-secativas (soja, mamona desidratado) ou não secativas (coco, mamona). A segunda classificação, amplamente utilizada, no caso de resinas alquídicas, é a que leva em consideração o teor de óleo presente na sua formulação (comprimento em óleo). Baseado nisso essas podem ser classificadas em curtas (com até 45% de óleo), médias (com 45 a 55% de óleo) e longas (acima de 55% de óleo).

Este tipo de sistema forma o filme (película dura após aplicação de uma tinta) não somente pela evaporação de solventes, mas também através de uma série de reações químicas complexas que se processam ao contato da resina com o oxigênio do ar e que envolvem processos de oxidação/polimerização (polimerização oxidativa) da parte insaturada da cadeia de ácidos graxos presentes na estrutura deste tipo de material. Estas reações também são conhecidas por cura ou secagem. A velocidade, das reações de polimerização oxidativa, pode ser modificada com a utilização de catalisadores metálicos, amplamente empregados na indústria de tintas e que são usualmente chamados de secantes.

THE RESEARCH AND DEVELOPMENT OF SOY PROTEIN AS AN INGREDIENT IN WOOD AND FIBER-BASED COMPOSITE ADHESIVES

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Research efforts to develop soy protein-based adhesives for wood and fiber-based composite products have increased in recent years. The impetus for increased research is the need to find value-added uses for soybeans and to develop more environmentally friendly adhesives that are not based totally on petroleum and natural gas-based (synthetic) chemicals. Furthermore, concerns regarding future crude oil supplies have compelled the wood industry to develop adhesives from renewable materials.

Reducing U.S. dependence on foreign oil will require significant increases in the domestic production of biobased fuels. Designing biofuel production systems that are economically, environmentally, and socially sustainable is an overarching goal of the bioeconomy movement. A key feedstock for the production of biodiesel fuel is soy oil. As a general rule, every bushel of soybeans yields 9 pounds of soybean oil and 51 pounds of soy meal. Most soy processors have significant opportunities for further processing and marketing the soy oil, but more limited opportunities for marketing the soy meal with the majority being used in animal feeding. This concern will limit the expansion of additional crushing of soybean for the oil that can be used in biodiesel manufacture. A 2004 United States National Renewable Energy Laboratory report (NREL, 2004) stated that “Soy oil supplies are limited and do not tend to expand with demand for biomass oils because they are byproducts. Only 19% of a soybean consists of oil while the remainder is sold as high protein animal feed. Any soy crusher will tell you that the demand for meal drives their production decisions and the oil is simply a byproduct. When asked if the demand for oil for energy use (biodiesel for example) can alter their decision pattern, the typical response is “unlikely.” In order for domestic soy oil supplies to increase significantly, there has to be a major increase in demand for soymeal.” Therefore, unless new, high-value industrial uses for soy meal are discovered and commercialized, there will be little incentive to increase its annual consumption.

Research of protein-based adhesives during the past decade has been mainly made with soy proteins primarily because of their availability and low costs. Most of this work has focused on the use of soy protein as an adhesive in wood and fiber-based composite applications. A wide variety of home building (sheathing, siding, etc.) and home interior (furniture, cabinets, doors, etc.) items are manufactured by the wood products industry. Some of the more common products used in the manufacture of these items include plywood, oriented strandboard, particleboard, medium density fiberboard, and a variety of molded wood products, all of which are made from veneer, flakes, particles, and/or fibers held together by industrial adhesives. The most commonly used adhesives are phenol formaldehyde-based adhesives for exterior-grade products and urea formaldehyde-based adhesives for interior-grade products. In the early stages of development, researchers found that many of the same issues that limited the use of soy protein-based adhesives with the advent of better performing synthetic are still true today, namely lower bonding strength and water resistance.

One of the methods that researchers use to improve the performance of soy protein-based adhesives is to use soy protein as a copolymer with synthetic resins. A US patent Reibel et. al., (1997) describes methods of preparing a soybean-based molding compound by cross-linking soy flour with methyl diphenyl isocyanate (MDI). Research by Dr. Roland Kreibich showed that by combining hydrolyzed soy protein with an adhesive currently used in end jointed lumber, phenol resorcinol formaldehyde (PRF), an adhesive could be developed that was cost competitive with PRF (Kuo and Myers, 2004). Furthermore, the adhesive had a faster cure time and could bond wood with higher moisture contents than PRF alone. Both of the aforementioned research accomplishments have been commercialized and are currently being used to make wood and fiber-based products in the United States.

These aforementioned discoveries provided the impetus to increase research efforts in many research laboratories to investigate ways to combine soy protein with other synthetic resins to develop new value-added adhesive systems. Researchers at Iowa State University replaced up to 70% of the phenol formaldehyde in adhesives with soy protein flour. The adhesives developed can be used to bond a variety wood and fiber-based composite products (Kuo, et.al., 2001, 2003).
In spite of the new technologies developed for soy protein-based adhesives, there has been limited commercial success. The use soy protein in the wood adhesive industry has always been primarily driven by the price of soy flour, relative to the synthetics. There is still a significant challenge to manufacture wood adhesives from soy protein at reasonable costs to meet stringent performance requirements. The future of soy protein in this market will be determined by price, the ability to capitalize on its unique properties such as cold setting and rapid water loss during bonding, and the improvement of the adhesive bond relative to water resistance. As these challenges are met

through further research, more commercial success can be expected.

To improve the performance of soy protein-based adhesives and to facilitate the transfer and commercialization of the technology, researchers at Iowa State University have focused on the development of soy protein hydrolysates as co-reactants with synthetic chemicals in soy protein adhesive formulations. Protein hydrolysis is one of the more important processes in the formulation of soy-protein-based adhesives for wood and fiber-based composite products. Protein hydrolysates produced from soy flour have been researched in the past for incorporation into chemical resin formulations for wood products as a means to decrease the petroleum content of adhesives used in the wood products industry. The hydrolyzed protein is reacted with synthetic resins such as phenol formaldehyde, phenol resorcinol formaldehyde, and melamine urea formaldehyde, to produce soy protein-based adhesives that can be used in a variety of wood and fiber-based products. Protein hydrolysis is used to reduce the molecular weight of the formulated adhesive facilitating wood penetration resulting in a stronger bond between the adhesive and the wood. Furthermore, protein hydrolysis helps reduce viscosity that will allow manufacturers to use their current equipment, such as spray systems, typically used to apply low viscosity resins to wood particles. In addition, short peptide chains expose more reactive sites compared to un-hydrolyzed protein, enhancing the reaction of the soy protein with the synthetic resin components in the adhesive formulation.

One hydrolysis procedure uses alkali at relatively high pH's (11-12) and temperature, typically approaching 140^{o}C requiring pressurization of the reaction vessel. Alkaline hydrolysis, however, is a random process; therefore "batch to batch" variation and the overall quality of the adhesive is difficult to control from the standpoint of viscosity and reaction with the other components in the formulation.

One way to eliminate the aforementioned issues with the alkaline hydrolysis method is with the use of enzymes. This alternative processing method has the potential to reduce the time, temperature and corrosive chemical consumption that will greatly improve the efficiency and safety of the process. Furthermore, because the enzymatic process is biological, it can significantly reduce the "batch-to-batch" variation in the hydrolysis process providing a more consistent hydrolysate. The protein hydrolysates produced using chemical methods typically are random and hard to limit or control. Hydrolysates produced with biological methods, through the use of enzymes, can be controlled both the type and extent of the hydrolysis. This process has proved feasible and Iowa State University has filed a patent application on this technology.

Studies examining the properties of the adhesives made with the hydrolysates show that the curing rate, water resistance and strength of the adhesives can be influenced by whether a chemical or enzymatically produced hydrolysate is used in the formulation. The research showed that hydrolysates produced using either chemical or biological methods can be used as ingredients in the adhesive formulations. The quality of the soy flour, however, can influence the performance the hydrolysate in adhesive formulations. The key quality factors include particle size, protein content and the level of protein denaturation. The research also showed that hydrolysates are compatible in both phenol and urea formaldehyde adhesives however, the compatibility of the hydrolysates in the formulations can be enhanced by the formulation of the synthetic resin used.

Researchers, including those at ISU, have shown that soy protein hydrolysate produced from soy protein flour, in combination with phenol and urea formaldehyde, can be used in plywood, oriented standboard, medium density fiberboard, and molded wood products. The goal of this research effort was to determine the feasibility of manufacturing soy protein hydrolyzates as an ingredient in these formulations. This presentation will discuss the research on soy protein hydrolysates as chemical reactants in synthetic wood and fiber-based composite adhesive applications.

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SOYINKS: PROCESSING AND MARKET

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Technology is available for manufacturing soy oil based printing ink vehicles with the desired commercial characteristics. Soybean oil and other representative commodity seed oils were heat polymerized in the absence of oxygen to yield exceptionally light colored and hydrophobic polymers that are used directly as non-petroleum vehicles to formulate lithographic news inks. Heat polymerized vegetable oil was mixed with monoester of an unsaturated fatty acid or a blend of unsaturated fatty acid monoesters for sheetfed and heatset ink vehicle formulations. In the formulation of the vehicle, unmodified vegetable oil was used as a third component. Esters were incorporated at a relatively low level, i.e. about 0.5-3.0% by weight of the vehicle. Heat polymerized and unmodified oil constitutes the major fraction of the vehicle, and thereby primarily is responsible for the rheological properties of the formulated ink. Biodegradation of these vehicles and inks were evaluated both by “Gravimetric Method” and “Modified Sturm Test.” With both methods our ink degraded faster and more completely than commercial inks. The United States Environmental Protection Agency (EPA) Method 24, 24A and Bay Area Method 30 are the three major methods used for VOC emission evaluation of printing inks. VOC of commercial inks and our ink formulations were tested and comparison of results from different methods were made. The results once again show the superiority of vegetable oil-based inks over petroleum inks. The recycling of both pre-consumer and post-consumer recovered paper is on the rise. The success of many paper recycling efforts depends on the “deinkability” of the printing products. Deinking studies were conducted at Western Michigan University, Kalamazoo, Michigan. Image analysis indicated that our soy ink (100% soy based) was removed more completely than commercial inks, even after six months of aging. The above technologies have been patented (U.S. Patents 5,122,188 and 5,713,990) and licensed to a major U.S. company.

Key words: soybean, oil, soyink, printing, vegetable

POLYMERS AND COMPOSITES FROM SOYOIL

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ABSTRACT

A wide range of high-performance, low-cost bio-based composite materials can be made using plant oils, natural fibers, and lignin. By selecting the fatty acid distribution function of plant oils via computer simulation and the molecular connectivity, we can control chemical functionalization and molecular architecture to produce linear, branched, or cross-linked polymers. These materials can be used as pressure-sensitive adhesives, elastomers, rubbers, and composite resins. This paper describes the chemical pathways that were used to modify plant oils and allow them to react with each other and various co-monomers to form materials with useful properties. When resins derived from natural oils are combined with natural fibers (plant and poultry), glass fibers, and lignin, new low-cost composites are produced that are economical in many high-volume applications. Plant oil is also a solvent for carbon nanotubes and nanoclays, permitting new high performance bio-based nanocomposites and coatings. These composites are used in agricultural equipment, automotive sheet molding compounds, civil and rail infrastructures, marine applications, housing, furniture and the construction industry.

KEYWORDS: Soy composite, natural fibre, Wood substitute

1. INTRODUCTION

Recently, Cara Plastics, in collaboration with the Affordable Composites from Renewable Sources (ACRES) program at the University of Delaware, has developed a broad range of chemical routes to utilize natural triglyceride oils (Figure 1) as a basis for polymers and composite materials.[1-11] These materials have economical and environmental advantages over petroleum-based materials making them an attractive alternative.

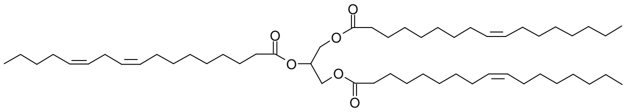

Figure 1. Triglyceride structure derived from plant oils, such as soy, corn, hemp, flax, peanut, sunflower, palm. Three fatty acids are connected to a glycerol center. (12-13)

2. COMPOSITE RESIN SYNTHESIS

Figure 2 shows typical chemical pathways which can be used to make the plant oils reactive in a time frame comparable to petroleum-based resins and these have been discussed in detail by Khot et al. The resulting low viscosity resin monomers can then be hardened by free radical or condensation type reactions, or combinations of the two, using typical catalysts and composite processing conditions. Some of these resins can also be derived using by-products of bio-diesel, such as glycerol (3-5). Others can be derived from the fatty acids of bio-diesel. For example, separation of the high oleic fatty acid content of bio-diesel provides a monomer feed stock for pressure sensitive adhesives (7), elastomers (10-Chapter 8), Coatings (10-Chap 8) and reinforcing rubber particles.

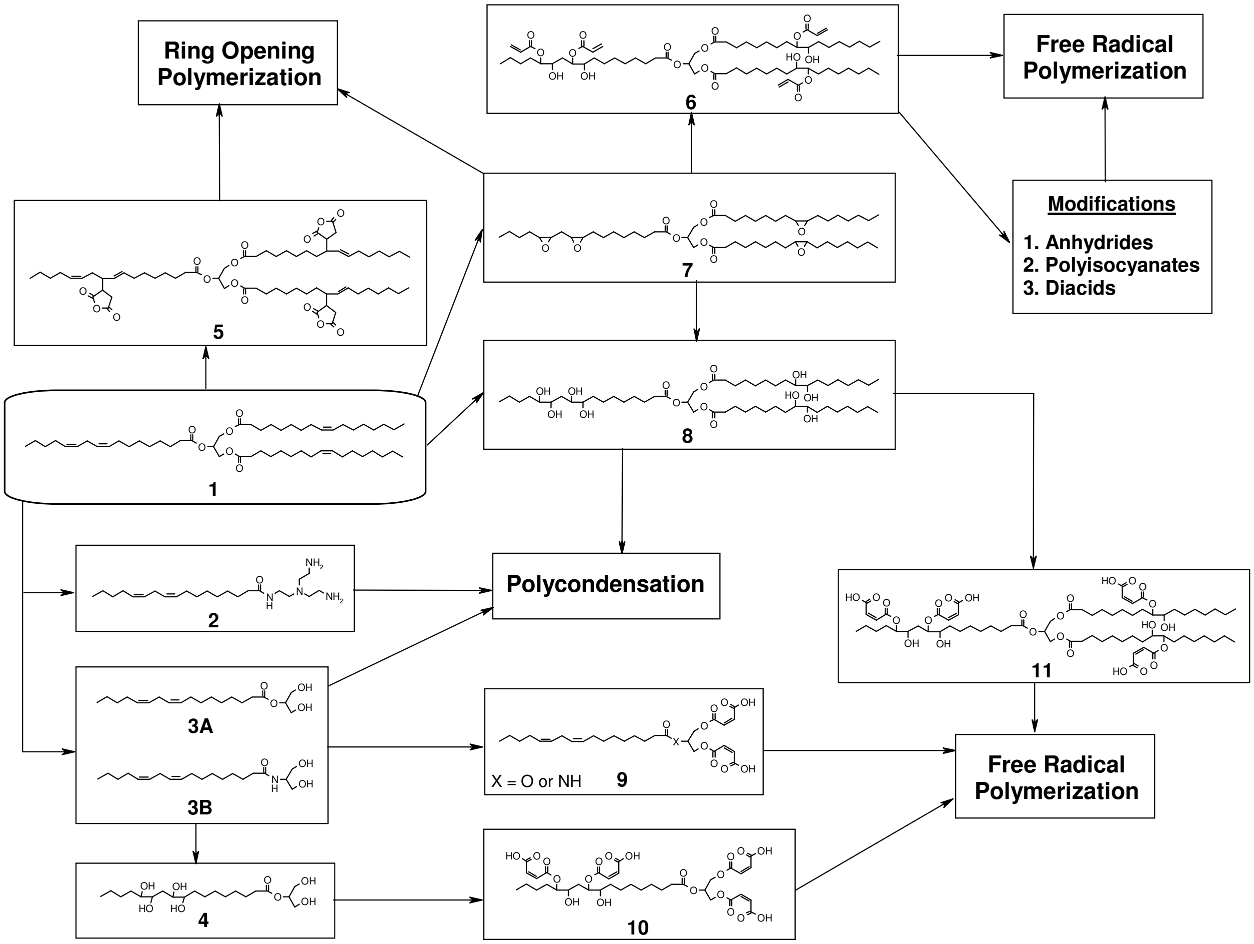

Figure 2: Reaction Pathways to convert plant oils to composite resins (1-3)

(5)

Such resins were first used in John Deere baler and tractor parts in 1999; 5 years later, these composites appear to be in excellent condition despite exposure to the harsh agricultural environment. In particular, the under-hood tractor parts (fan blade cowlings) showed excellent property retention.

4. HIGH-SOY SHEET and BULK MOLDING COMPOUND

The soy-based resins can be modified to make SMC and BMC containing a high soy fraction, as demonstrated by Lu and Wool (28-29). By adding 2-3 moles per triglyceride of maleic anhydride (MA) to the hydroxyl groups remaining in the Hydrolylated Soyoil, or Acrylated Epoxidized Soybean oil (AESO), the MAESO is produced. The pendant carboxyl groups created by the addition of MA are then combined with divalent cations such as MgO or CaO to thicken the resin with the fibres and catalyst. Since AESO has a functionality of $f \approx 3\text{-}4$, the addition of MA raises the value of f to 5-6, and we obtain the optimal properties for this high-soy. The flexular and tensile properties of MAESO resin compare favourably with petroleum-based resins, as shown in Figure 3. When placed in a heated mold, the SMC viscosity decreases as the divalent cation-carbonyl oxygen bonds break, flow occurs to fill the mold and the curing reaction proceeds to produce a high performance soy-based SMC composite. The soy SMC can also be made with natural fibres (flax, feather), in addition to chopped glass fibres and carbonized chicken feathers (10). This high-soy resin is currently being manufactured by Cara Plastics in Illinois.

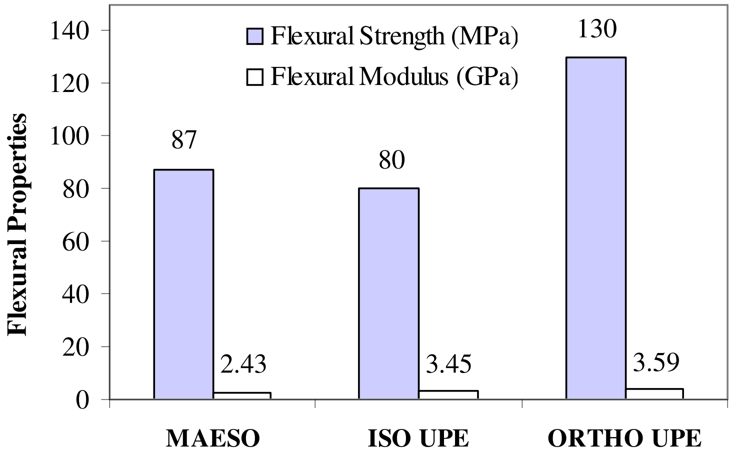

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Figure 3. Flexural Properties of MAESO compared to commercially available unsaturated polyester resins (UPE)

5. HURRICANE RESISTANT HOUSES

In recent years, the United States was hit by several major hurricanes, Katrina (2005), Hugo (1989), Andrew (1992), and Iniki (1992) causing over $27.5 billion dollars cumulatively in damage to insured property [2]. In 2004, the damage from the four hurricanes which impacted Florida (Charley, Frances, Ivan and Jeanne) reached at least $30 billion dollars and according to the NOAA hurricane forecasters, there exits an ominous potential for continued hurricane damage in the next several decades. Typically, when houses are exposed to hurricane forces, roofs are most susceptible to damage, followed by walls and openings, and then foundations. The development of hurricane resistant housing by the ACRES group was prompted by a visit from a South Carolina congressional delegation to the laboratories at the University of Delaware; two back-to-back hurricanes had just created considerable damage in that state. The problem was posed: could we use the new low cost green materials to develop high performance housing structures that would be more hurricane resistant? Given the level of devastation and the multibillion dollar costs, the solution appeared daunting, especially if the new housing materials should be made with paper, straw, chicken feathers and soybeans. However, upon examination of the nature of the damage, it was clear that the engineering solution was not that complex but would require a radical new approach to both the roof design and method of construction. Inspection of the damage in South Carolina and Florida in the aftermath of Hurricane Andrew revealed that most of the damage to roofing was not of a catastrophic nature, but rather a gradual process of removing particle boards from the roof by the wind-induced pressure drop: as the hurricane winds sweep over the roof at 150 mph (Category 5), the roof acts like an imperfect airfoil and creates a vacuum on the sheltered or lee side of the roof. This vacuum is only of the order of 1 psi (max vacuum is 14.7 psi), but this is sufficient to peel off the 8x3 foot particleboards, which are nailed to the joist boards of the A-frame substructure. By comparison, a Boeing 747 jumbo jet takes off and lands at 200 mph with only a pressure drop of about 1 psi on the top side of the wings. The force to peel off the particleboards is proportional to the square root of the number of nails holding them in place. Thus, the solution involves the following: either use an enormous number of nails or make the whole roof as a monolithic piece, such as the airfoils used in aircraft wings, or, the molded hull of a boat. The ACRES group with Cara Plastics personnel addressed this engineering problem with bio-based materials. The basic concept for the roof design in shown in Figure 4 and consists of a foam core composite structure with an integrated webbing of I-beams in the foam core (20,21). This particular application of bio-based composites to housing is potentially the world's largest utilization of fibers and resins from renewable resources. When bio-based resins derived from natural oils are combined with natural fibres (plant and poultry), glass fibres, and lignin, new low-cost composites are produced that are economical in many high-volume applications, such as houses and furniture.

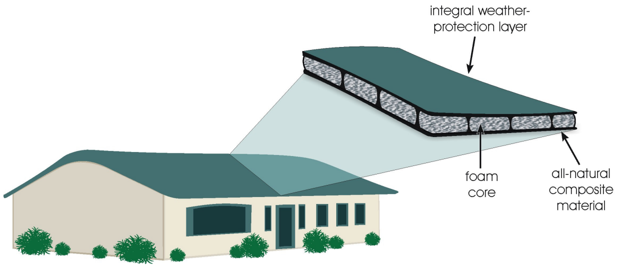

Figure 4 Foam–core roof of a hurricane resistant house made with waste paper, feathers and soybeans.

The composite is made with cellulose fibres derived from waste paper and cardboard, chicken feathers and infused with soy resin.

The surface weather layer can be made with a nano-clay reinforced soy gel coat (24). The 10 inch thick closed-cell foam can also be made with soyoil resin (AESO) using a CO_2 blowing agent (10,33). The above design for hurricane resistant roofs can be modified to make emergency shelters suited to survivors of tsunamis, floods, hurricanes and other disasters (10). These are ultra light weight, low cost structures that can be rapidly deployed around the world as needed for emergencies.

CONCLUSIONS

Bio-based Composites can be readily made with natural fibers and soy-based resins. The chemistry, physics and manufacturing engineering is now quite well understood and is summarized in reference 10. They have properties that are comparable to petroleum based resins and at reasonable cost. The composites with natural fibers have very low cost since most of the reinforcement (recycled paper and chicken feathers) are inexpensive, which therefore makes them most suited to new high volume applications, such as housing with new and improved properties. These green materials are highly sustainable and will have significant impact on the environment. Given the demise of the oil industry in about 25 years, the move towards new bio-based composite materials should gain high acceptance (price-wise) in the next decade. Mass production of these bio-based resins begins in early 2007 with Cara Plastics (www.caraplastics.com)

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TECHNOLOGY TRANSFER: PUBLIC AND PRIVATE RESEARCH AND COMMERCIALIZATION PARTNERSHIP IN THE UNITED STATES

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Today, America's food and agricultural producers operate in a global, diverse, and highly competitive marketplace driven by consumers worldwide. American farmers are among the most productive in the world and our food and agricultural system provides the nation with the safest, highest quality, and lowest cost food and fiber anywhere. Much of the credit for this success belongs to our public research system and its success in generating new knowledge and technologies that improve productivity and develop new markets for agricultural products. The Department of Agriculture helps drive continuous innovation through science and technology by forming research and commercialization partnerships with other public research institutions and the private sector.

The Office of Technology Transfer (OTT) in USDA's Agricultural Research Service (ARS), is key in facilitating these partnerships and in transferring research outcomes for broad beneficial use by the public and agricultural industries of the U.S. and other nations. Many of these research outcomes include patented or otherwise protectable technologies. These partnerships include private sector corporations as well as universities (i.e., other public sector institutions). The mechanisms ARS uses to commercialize technologies have evolved over the past 25 years in concert with Federal legislation that governs Federal and non-Federal researchers. Federal, state, and private sector researchers are all working toward the same goal of adopting research results and creating products and services. However, the missions, geographical scope, and accountability to our respective institutions create some real challenges.

This paper describes the "roots" of technology transfer in the U.S., the culture of ARS technology transfer, and some observations on how the intersection of technology transfer authorities has led to convergence as well as divergence among Federal and non-Federal agricultural researchers in the public sector. Furthermore, some metrics and successes in technology transfer in ARS --- some involving partnerships, others strictly in USDA --- are provided as illustrations. Finally, we offer a glimpse of what we believe is the future direction of agricultural research, also including discussion on the non-food uses of agricultural products in industry (e.g., biofuels, etc.)

The "roots" of technology transfer can be traced to the earliest activities that can be defined broadly as "agricultural research" in the U.S. Specifically, in 1819 and 1827 the Secretary of the Treasury directed consular and naval officials to transport useful seeds and plants to the U.S. (Dept. of Treasury Circulars; see Shurtleff and Aoyagi 2004 Agricultural Experiment Stations: Work with Soy on the web at: (www.thesoydailyclub.com/SFC/USDA61a.asp). The subsequent western expansion during the 19th Century resulted in the creation of the "Section of Foreign Seed and Plant Introduction" in 1897 (see Shurtleff and Aoyagi 2004). Additionally, in 1839, the Patent Office established an Agricultural Division to conduct research. Congress designated $1,000 for "collecting and distributing seeds, carrying out agricultural investigations, and procuring agricultural statistics." (National Archives and Records Administration (RG 07-18), on the Web at http://www.nara.gov/).

Federally-financed R&D and technology transfer in agricultural research dates from May 15, 1862, when President Abraham Lincoln signed a bill that established the Department of Agriculture, or as he coined it, "the People's Department." The Act also instructed that the "*Commissioner of Agriculture…acquire and preserve…all information concerning agriculture*…" Related bills enacted at the same time included The Homestead Act in 1862, and the Morrill Acts of 1862 and 1890 that led to the establishment of major state operated agricultural research centers. State Experiment Stations (SAESs) were first established in Connecticut and California in 1875 based on the German model of experiment stations observed by American scientists. The Hatch Act of 1887 later authorized one for each state. Finally, the "Equity in Educational Land - Grant Status Act of 1994," (sometimes called the Tribal Colleges Act) brought Native American schools into the fold. (For a comprehensive review of these enabling legislations cited above, see the website for the National Association of State Universities and Land Grant Colleges (NASULGC) at http://www.nasulgc.org). Thus, the Federal Government and the States established an infrastructure for publicly-funded agricultural research throughout the U.S. to conduct research, and ultimately to transfer results to the public. Today, the collective results of these legislative Acts have created the 133 Land Grant Colleges and Universities. Although USDA scientists have conducted research since the 1860s under various departmental structures, the Agricultural Research Service (ARS) was formally established in 1953. Today, many of our more than 100 ARS facilities are co-located at these institutions and we collaborate on many research projects.

Various legislative authorizations over the past 27 years created incentives for the government, universities, and industry to work together to commercialize new technologies for the public benefit. *Extramural research* funded by Federal appropriations are managed according to the Bayh-Dole Act of 1980 that allows institutions performing the research to take title to their inventions and to license rights to practice the inventions without constraints and without notifying the public. In contrast, inventions arising from *intramural research* conducted by Federal agencies, such as ARS, are governed by the Stevenson-Wydler Act of 1980 and subsequent legislation, especially the Federal Technology Transfer Act of 1986 and other more recent legislation.

Collectively, this legislation frames the functions and actions of our Office of Technology Transfer (OTT). We coordinate the technology transfer activities in ARS, and have the authority to develop and sign a very specific Federal instrument for partnerships, specifically Cooperative Research and Development Agreements (CRADAs). We also represent the Secretary of Agriculture on intellectual property (IP) management, and have the sole authority for licensing any inventions developed within any of the USDA agencies conducting intramural research, including the U.S. Forest Service, the Food Safety and Inspection Service, and the Animal Plant Health Inspection Service. OTT consists of approximately 43 full time equivalent (FTE) employees, with about half located at the ARS headquarter facilities in the George Washington Carver Center, in Beltsville, MD. The Office is centralized in policy and approvals, marketing, and licensing, and decentralized in the negotiation and implementation of cooperative research agreements. ARS has eight in-house registered patent agents, and all patent applications and prosecutions are conducted by permanent ARS employees, providing extraordinary continuity of highly professional services throughout the patenting and licensing process. Also key to our successes is the distribution of 7 Technology Transfer Coordinators (TTC), stationed among the eight Area Offices across the nation that manage the execution and quality of the scientific research conducted at over 100 locations. TTC's facilitate cooperative research of their regional scientists with public / private partners, but maintain a national perspective to these partnerships.

To evaluate the implications of the various legislative Acts to our partnerships, we need to frame the context of the Agricultural Research Service policies of today. ARS integrates technology transfer within its research mission, protecting intellectual property when necessary to *facilitate* technology transfer. However, we favor public releases of plant varieties, and avoid patenting "animals" or research tools, and because we are a public research institution, we promote further research by permitting license-free research with any ARS technology. Consequently, the decisions we make relative to licensing Federal technologies are governed largely on the goal of facilitating technology transfer for public good in support of U.S. agricultural businesses, not a goal of generating revenue for research.

In licensing IP, there are two mechanisms which have processes highly prescribed by Federal statute. First, (also in reference to CRADA involvement) "background inventions" are those that are made by Federal researchers under normal intramural research authority with Congressionally-appropriated funds. If a potential licensee requests exclusivity, then we must publish a Federal Register notice of our intent to license the specific patent to the applicant company. The purpose is to inform the U.S. public so that other qualified individuals or businesses who also want a license to the technology have an opportunity to object to the exclusivity. We then must address all objections, and that may result in co-exclusive licenses, or exclusivity by field of use, or in rare circumstances, non-exclusive licenses to all objectors who submit qualified license applications. All of this is prescribed in 37 CFR 404 (Licensing of Government Owned Inventions), and we are diligent in following proper procedures. Federal agencies cannot deny a license to applicants that meet minimum qualifications, except that --- all other factors being equal --- agencies can grant preferential license to a small U.S. business, but cannot select one small business over any other. Furthermore, even licenses to foreign owned companies require "… substantial manufacture…" of the products in the U.S.

The second mechanism relates to IP developed under a CRADA with a non-Federal partner --- almost always a private sector company. This is also a prescribed procedure, but by statute and not by the Code of Federal Regulation (15 U.S.C. 3710a). Inventions made under a CRADA are a distinct advantage for the private sector company for two reasons. First, the company has the right to negotiate an exclusive license to at least one predefined field of use without Federal register notice. Therefore, their competition is not only excluded, but remains uniformed. Second, federal agencies can exempt jointly developed data from Freedom of Information Act requests for up to five years, but in practice, ARS rarely grants confidentiality for more than one year. Universities have greater flexibility in licensing to local / regional companies, whereas Federal agencies have to justify processes to the taxpayers of any given state as well as to the taxpayers of the other 49 -- therefore, preferential licensing by the government is not permitted.

Despite some of the difficulties described above, these legislative acts have produced beneficial solid relationships. ARS has approximately 200 active CRADAs with the private sector, and separately, over 2,000 cooperative projects with universities where Bayh-Dole rights apply. A total of 335 active licenses are producing 100 products available to the public. Over 125 of these licenses are executed with universities to consolidate rights; 27 of these are producing products from utility patents, plant patents, and Plant Variety Protection Certificates. Thus, there is a demonstrable benefit to the public, to the inventors, and to the publicly-funded research institutions conducting the research. Recognizing that agricultural markets are characterized by thin profit margins requiring exclusivity of rights to protect investments, the majority of our licenses are exclusive; at least 40 percent of these licenses are with small businesses. Our licensees are increasingly successful at producing products with these exclusive rights to our inventions. This presentation highlights some of those current successes, including a technology over the past several years that prevents cut fruits and vegetables from turning brown, development of restructured fruit bars using a technology for making 100 percent fruit bars from pureed fruit, a peanut butter substitute that uses sunflower seeds (and avoids peanut allergies in children), and a number of new table grape varieties that can also be raised by foreign grape growers.

A technology most relevant to this meeting is a biodegradable hydraulic fluid made from soybean oil, which is now being used to power the Statue of Liberty's elevator. Until recently, the Statue's elevator used mineral oil formulations derived from petroleum-based stocks. The National Park Service contacted ARS scientists requesting development of a biobased fluid for use in the statue's elevator. The Park Service wanted a product that was environmentally friendly, produced from a renewable resource, that was economical and nonpolluting, and met all industry standards for safety and performance including viscosity, stability, and flame resistance. ARS researchers already had the know-how to develop this technology. Though other vegetable oils would work, soy oil was chosen because of its low cost, chemical versatility, and availability as a renewable, home-grown resource. Soy is the leading U.S. source of food-grade oil, yet only 517 million pounds—3 percent of the total supply, is used for industrial purposes. The invention, jointly developed with Pennsylvania State University, was licensed to a start-up company that was immediately acquired by Bunge, a global food and agricultural commodity company, in early 2006, and first sales were reported by mid-2006.

Where do we go from here? To see the future, we need to look to the past. In the 1930s, we were using ethanol to power our cars, and biobased products were early concepts. Henry Ford predicted in 1937, that "… almost all cars will be made of such things [soy plastic]." In 1940 he installed a plastic trunk lid on one of his personal cars, demonstrating its durability with the blow of an axe. A year later he built an all soy plastic car which was hailed as a"…outstanding industrial achievement." (From the Henry Ford Museum http://www.hfmgv.org/exhibits/hf/facts.asp). This innovative development in research and development was called "chemurgy". (Old Efforts at New Uses: A Brief History of Chemurgy and the American Search for Biobased Materials, Mark R. Findlay, Armstrong Atlantic State University, Savannah, GA 31419, USA, 2004 by the Massachusetts Institute of Technology and Yale University and can be found on the web at: http://www.mitpressjournals.org/doi/pdf/10.1162/108819803323059389). Findlay's scholarly article written for the Journal of Industrial Technology captures most, if not all the sources for information on Chemurgy and the "new uses' movement. Unfortunately, cheap oil sent the U.S. and other nations, and their research efforts in another direction. In the context of today's issues, the times are indeed changing.

Obviously, Brazil, the U.S., and most of the world now recognize an urgent need to become less reliant on imported oil. Biofuels may help achieve those goals, and the adoption of biobased products can "back out" petroleum usage through substitution with agricultural products. Crops that are good for the environment and rural communities that also reduce our dependence on imported fossil fuels are new priorities. There is renewed hope that with continuing agricultural research and the private/public partnerships created – both national and international --- the products produced from agricultural materials are limited only by our imagination. I am confident that the most prosperous era in global agricultural history is dawning to meet the continuing and expanding needs of the public.

BIOENERGY MARKET DEVELOPMENTS IN THE WORLD – DEVELOPMENT, STATUS, AND TRENDS

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Since mid 2005, agriculture commodity based raw materials start competing with petrol on energy value. Palm oil and soybean oil have equal or lower price than petrol when calculated on energy content. This has created an enormous momentum for new bioenergy investments in biodiesel, bioethanol as well as in biomass. This has pushed governments allover the world to look again at the policies and support systems to be put in place for creating a market for bioenergy. The latest interim conclusions on global warming are only pushing this evolution to a higher level. New ambitious targets are being set for carbon dioxide reduction levels in various parts of the world. Bioenergy is a corner stone of such policy decisions.

While biodiesel is not new and already started in Europe 15 or more years ago, it was mainly the introduction of the Biodiesel Standard EN14214 and the introduction of the Biofuel Promotion Directive (both in 2003) that have generated the strongest push for exponential market growth. The bioethanol market was first developed in Brazil more than 20 years ago. However, it was the US market that has opened this segment a couple of years ago for large scale investments. Standards also followed in the US for bioethanol and biodiesel. Today both biofuels are growing at a tremendous pace throughout the world. The technical advantages brought on engine lubrification (biodiesel in ULSD) and on reduction of exhaust emissions (biodiesel as well as bioethanol) also helped of course. Major trigger to make this happen, apart from the more attractive raw material price position is the availability of tax incentives, which come in very different forms.

Without these three elements – a proper fuel standard; a technological fit and environmental advantage; a favorable tax environment – the market growth could never have been so successful for biodiesel and bioethanol. However, having said this, these three constraints could also be the weakness of some of the biofuels in the future. Raw material pricing and tax incentives are only sustainable in a short term. As we already see today, the strong demand for corn, - the major raw material used in the US for bioethanol - and the worldwide demand for vegetable oils & fats for biodiesel have already driven starch-carbohydrate and oils & fats prices to new heights. Today, biodiesel production margins are further reduced by the recent shrinking price for petrol. In longer term, technology and economics should bring the sustainability.

Although the treat of a strong petrol price reduction could be severely damaging on very short term, it is estimated to be only a short-term price change, and as such seen as a temporary phenomenon. Today, carbohydrate and vegetable oil prices are more and more linked to petrol price, which fuels the debate on “Ag products – Food and/or Fuel” and on “Sustainable production of raw materials”. But this again is a trigger to start developing new starch and oil crops dedicated to energy production, such as for example Jatropha that can be grown on new agriculture land. Similarly, the debate on “Food or Fuel” also could be a major trigger to support developing markets in increasing yields for agricultural products by using better technology as well as better post-harvest handling, reducing the losses which are unfortunately sometimes higher than acceptable.

On mid term it can be expected that new biofuels will hit the market. Biomass to liquid and similar developments based on gas or coal will be the first new products coming to the market. Processing to hydrogen and hydrogen fuel technology remains a promise for the longer term. On mid-term, fermentation processes using waste materials will generate key chemical building blocks such as methane, ethane, methanol and ethanol to be used as raw material for novel biofuels. Synthetic fuels are already been produced from natural gas using the Fischer-Tropsch process. Building blocks such as methane produced from biomass will be converted to such synfuels or syngas as well. Industrial scale plants are already operational testing economics and sustainability of this approach. These products will have equal or superior quality to diesel or gasoline and probably fit better with the increasing demand for cleaner burning fuels. Will this result in a short life cycle for the current biofuels? Probably not. Too many changes in production and in use are needed to introduce new products. The market stakeholders involved will weight he effects for every new development in a detailed and properly controlled way before pushing forward.

During the presentation, a review of the bioenergy market will be given with a targeted look at current evolutions and future developments. The presentation will also bring a proposal to join efforts in looking at possible strategies in developing and managing these new bioenergy production systems.

PESQUISA E DESENVOLVIMENTO NA UFRGS E PERSPECTIVAS DE UTILIZAÇÃO DE ÓLEOS VEGETAIS COMO ALTERNATIVA À PETROQUÍMICA NO BRASIL.

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key words: soybean oil, polyol, polyurethane, epoxi resin, biodiesel, organic-inorganic hybrid
palabras-chave: óleo de soja, poliol, poliuretanas, resina epóxi, biodiesel, híbrido orgânico-inorgânico

Introdução:

Em 1996 através do convênio firmado entre a UFRGS e o governo do Estado do Rio Grande do Sul iniciou-se o projeto *“Ampliação da base tecnológica da UFRGS para promover a extração de bases oleoquímicas”* que envolveu, além do Instituto de Química, Instituto de Ciência e Tecnologia dos Alimentos, Escola de Engenharia - Dep. Eng Química, Escola de Administração. Este convênio foi o passo inicial para o estabelecimento da área de pesquisa em Oleoquímica dentro do Instituto de Química da UFRGS. Nesta área são desenvolvidas pesquisas que visam a modificação química de óleos vegetais de forma a utilizá-los como matéria-prima na fabricação ou formulação de novos produtos como poliuretanas, resinas epóxi, plastificantes para PVC, isolantes e adesivos, entre outros, bem como na área de extração e caracterização de óleos essenciais e vegetais.

Paralelamente com a implantação do Programa Nacional da Produção e Uso de Biodiesel (PNPB), foi criado na UFRGS o Grupo Multidisciplinar de Pesquisa e Desenvolvimento em Biocombustíveis que congrega, além dos pesquisadores do Instituto de Química, pesquisadores da Faculdade de Agronomia, da Escola de Engenharia-Departamentos de Engenharia Química e Engenharia Mecânica, da Escola de Administração e do Centro de Biotecnologia.

Nesta apresentação serão abordados os trabalhos desenvolvidos no Instituto de Química na área de modificação química de óleo de soja e as atividades realizadas pelo Grupo Multidisciplinar de Pesquisa e Desenvolvimento em Biocombustíveis.

DISCUSSÃO:

MATERIAIS HÍBRIDOS ORGÂNICO-INORGÂNICOS [1]

Materiais híbridos orgânico-inorgânicos podem ser preparados através do processo sol-gel e têm aplicações em diversas áreas tais como: biomateriais, catálise, óptica, membranas, cromatografia, eletroquímica, revestimentos de superfícies metálicas. Óleos vegetais podem ser utilizados como componentes orgânicos na preparação desses filmes híbridos e, por serem biodegradáveis e oriundos de fontes naturais e renováveis, constituem-se em interessante matéria-prima do ponto de vista ambiental. O objetivo deste trabalho foi obter filmes híbridos orgânico-inorgânicos a partir de diferentes óleos de soja funcionalizados para serem utilizados em revestimentos de proteção à corrosão de superfícies metálicas, em substituição aqueles à base de cromo. Foram utilizados como precursores orgânicos o óleo de soja epoxidado (OSE) e óleos hidroxilados obtidos pela reação do OSE com ácido fórmico (OSH), etilenoglicol (OSHG) e meso-eritritol (OSHmeso). Esses precursores orgânicos foram combinados com tetraetoxissilano (TEOS) ou com a mistura 3-aminopropiltrietoxissilano (APTES)/TEOS por hidrólise in situ do precursor inorgânico. Neste trabalho otimizaram-se as condições reacionais para a obtenção dos filmes híbridos, variando-se as proporções dos constituintes (precursor inorgânico, óleo de soja funcionalizado, água e solvente), a natureza do precursor sol-gel, o tempo de pré-cura e a taxa de aquecimento no processo de cura. Os filmes macroscopicamente homogêneos foram caracterizados por RMN de ^{29}Si, espectroscopia de infravermelho com transformada da Fourier utilizando reflexão total atenuada (ATR-FTIR), termogravimetria (TGA), gravimetria, microscopia eletrônica de varredura (MEV), inchamento em hexano e extração em tolueno, adesão e dureza. Os filmes híbridos que apresentaram as melhores características considerando os resultados dos testes de adesão, dureza, inchamento e extração foram os sistemas óleo de soja hidroxilado com valor de OH igual a 198 e TEOS e o óleo de soja epoxidado modificado com 3-aminopropiltrietoxissilano e TEOS.

POLIURETANAS E COMPÓSITOS [2,3,4]

A transformação de óleos vegetais em polióis, matéria-prima para a obtenção de poliuretanas, é uma excelente alternativa para a preparação de biomateriais e biocompósitos. Devido à sua compatibilidade com diisocianatos e à sua viscosidade, os polióis oleoquímicos são particularmente interessantes em sistemas poliuretânicos livres de solventes, de dois-componentes ou compósitos, largamente empregados como revestimentos decorativos ou protetores. Este trabalho teve por objetivo o estudo da preparação e das propriedades de poliuretanas (PUs) obtidas a partir de polióis de óleo de soja contendo diferentes índices de OH com três diferentes diisocianatos: diisocianato de tolileno (TDI), 4,4-diisocianato de difenilmetano (MDI) e 1,6-diisocianato de hexametileno (HDI). Foi, também, estudada a preparação de compósitos de poliuretanas obtidas a partir de polióis de óleo de soja e TDI e cargas naturais. Utilizaram-se como cargas xisto retortado(XR), em diferentes porcentagens mássicas, e cinza de casca de arroz (CA) com porcentagem mássica de 10%. Poliuretanas obtidas a partir de polióis epóxi-formiato com funcionalidade de 1,9 a 3,2 resultaram em materiais termofixos com diferentes densidades de reticulação e temperaturas de transição vítrea desde 1 até 48°C. As poliuretanas preparadas com isocianatos aromáticos, MDI e TDI, (cadeia rígida) apresentaram Tg levemente superior ao polímero obtido com o isocianato de cadeia flexível. A Tg não sofreu nenhuma variação significante em relação ao tempo de cura entretanto, observou-se uma Tg maior para o polímero obtido a temperatura mais alta (100°C), que pode estar associada a uma reação de polimerização dos grupos epóxidos residuais no poliol. A temperatura inicial de decomposição da PU foi a mesma para todos os polímeros (cerca de 210°C), sugerindo que a degradação inicia pela ligação uretana. A presença de grupos formiato no poliol acelera a degradação térmica da PU em relação à PU petroquímica. Compósitos de poliuretana com cargas que são resíduos de processamento e abundantes no Brasil (xisto retortado, XR, e cinza preta de casca de arroz, CA) foram obtidos. Os compósitos de XR apresentaram, propriedades semelhantes ou superiores à da PU sem carga. Entretanto, o aumento de XR fragilizou a amostra levando à diminuição da elongação, mostrando que embora haja uma interação polímero/carga, a interação matriz polimérica/carga não é muito boa. O compósito preparado com 10% de CA apresentou melhores propriedades que o compósito de mesma proporção mássica de XR e que a PU sem carga. Sugerindo, assim, uma melhor interação da cinza preta de casca de arroz com a matriz polimérica quando comparado ao xisto retortado.

RESINAS EPÓXI [5

Óleo de soja epoxidado foi curado com os anidridos: dodecenilsuccínico (DDS), maleico (MAL), ftálico (FTA), succínico e hexahidroftálico (CH). As reações foram iniciadas com aminas terciárias tais como trietilamina (TEA), N,N'-dimetilanilina (ARO) e 1,4- diazobiciclo[2,2,2]octano (DABCO).

As propriedades mecânicas e térmicas das resinas epóxi curadas usando TEA como iniciador foram investigadas por análise térmica dinâmico-mecânica (DMTA) e termogravimétrica (TGA). Todas as amostras apresentaram características de materiais termofixos. Os materiais termofixos obtidos a partir de anidridos com estruturas rígidas (FTA, MAL e CH) mostraram alta temperatura de transição vítrea e densidade de reticulação. Quando um excesso de grupos epóxido foi usado (R= 0,5), a temperatura de transição vítrea do material diminuiu. As resinas epóxi exibiram estabilidade térmica até 300ºC. O grau de epoxidação do óleo de soja influencia as propriedades mecânicas e a temperatura de transição vítrea, quanto maior o conteúdo de grupos epóxido, maior é a Tg e a dureza do material. As resinas epóxi preparadas a partir de óleo de soja epoxidado mostraram excelente resistência química em NaOH e ácido sulfúrico, mas degradaram-se facilmente quando em contato com solventes orgânicos (tolueno, acetona, gasolina e etanol).

HIDROFORMILAÇÃO DO ÓLEO DE SOJA [6,7]

Neste trabalho estudou-se a hidroformilação de ésteres graxos insaturados, utilizando-se o complexo $HRh(CO)(PPh_3)_3$ como catalisador. As reações foram otimizadas utilizando-se o oleato de metila (OM) como substrato padrão. Para este éster obteve-se 100% de conversão e 90% de seletividade em aldeídos. As condições reacionais otimizadas para o OM foram aplicadas na hidroformilação do óleo de soja, obtendo-se 100% de conversão e 85% de seletividade em aldeídos. A hidroformilação/aminação redutiva do óleo de soja foi realizada utilizando-se uma diamina primária (dianilina). Nesta reação, observou-se a formação do intermediário imina, mas não foi possível realizar a hidrogenação deste grupamento para obter-se a respectiva amina.

Neste trabalho, uma série de rotas sintéticas foram avaliadas para a obtenção de diferentes ligantes contendo grupos de poli(etilenoglicol) em suas estruturas, visando a aplicação destes na hidroformilação bifásica de olefinas. A obtenção da fosfina FOFPEG, somente foi possível após desenvolver-se uma metodologia composta por 5 etapas. Os ligantes FOTHPEG e FOTPHPEG, foram obtidos com altos rendimentos através da reação do composto HPEG com PCl3 ou PhPCl2, na presença de trietilamina e THF. Os testes catalíticos destes ligantes com cadeias de PEG, utilizando-se o sistema PEO-400/n-heptano com complexos de ródio, indicam que há a formação de espécies ativas para a hidroformilação bifásica de diferentes olefinas. Na hidroformilação do 1-hexeno com RhCl3.3H2O/FOTHPEG, conseguiu-se realizar 10 reciclagens do sistema catalítico, sem perda na atividade.

BIODIESEL [8-15

De forma integrada as atividades que vêm sendo realizadas pelo **Grupo Multidisciplinar de Pesquisa e Desenvolvimento em Biocombustíveis** referem-se ao desenvolvimento de sistemas de produção (sucessões ou rotações de culturas), processamento pós-colheita e pré-processamento industrial, competição de cultivares, adaptação e manipulação genética para a melhoria de produtividade, avaliação de equipamentos para processamento industrial, otimização dos processos produtivos de biocombustíveis, caracterização química e físico-química dos biocombustíveis no Centro de Combustíveis, Biocombustíveis, Lubrificantes e óleos (CECOM), estudos de novas aplicações para a glicerina, como biopolímeros, avaliação e simulação de processos de produção de biodiesel, pesquisas experimentais e de campo com uso de combustíveis GNV+Diesel, Diesel e Biodiesel em tratores e motores. Em consonância com os avanços técnico-produtivos, são desenvolvidas e validadas modelizações de sistemas e configurações de produção e gestão de propriedades rurais familiares e de cadeias agroindustriais de biocombustíveis.

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FERULOYLATED SOYBEAN OIL: NOVEL SOY-BASED COSMECEUTICALS

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Cosmeceutical, a combination of cosmetic and pharmaceutical, is a marketing non-regulated term coined in the past decade to imply a cosmetic or skin-care formulation that contains one or more active ingredients that impart a physiological or biological “medicinal” benefit to the consumer. The term is often used in cosmetic advertising to promote products containing antioxidants, vitamins, phytochemicals, or enzymes, which the manufacturer claims impart a health benefit to the user.

We have synthesized novel, lipid-based cosmeceutical ingredients by incorporating ferulic acid onto the glycerol backbone of soybean oil. Ferulic acid is present in nature esterified to other plant components, such as the hemicellulose and lignin fractions of plant cell walls, as well as in the waxy surfaces of leaves and occurs naturally in our food supply. Ferulic acid has a maximum UV absorbance at 322 nm, which falls between the UVB and UVA regions, making it a broad UV absorber. Ferulic acid also possesses excellent antioxidant properties, double the antioxidant capacity of ascorbic acid and alpha-tocopherol. Ferulic aid would be a preferred cosmeceutical ingredient except for its low solubility in organic phases and its propensity to yellow when applied to the skin. We were able to deliver the cosmeceutical benefits of ferulic acid to cosmetic and skin-care formulations through its esterification to soybean oil.

The transesterification of soybean oil with ferulic acid ethyl ester adheres to the tenants of green chemistry. The synthesis was conducted using a backed-bed bioreactor with soybean oil as the solvent. The lipase catalyst was recycled over an eight week period, and byproducts were separated and subsequently converted to product. The resultant feruloylated soybean oil (F-SBO) possesses broad range UV absorbance (290 to 370 nm) and antioxidative properties, making it a potential substitute for petroleum based cosmeceutical ingredients. Applications and commercialization of the patented F-SBO will be discussed.

The UV absorbing efficacy of the F-SBO was greatly improved by its encapsulation as microdroplets within a starch matrix via steam jet cooking. Irradiance measurements through thin films of starch-encapsulated F-SBO showed improved UV absorbance and stability using half the quantity of F-SBO than the non-starch encapsulated F-SBO.

Key words: Biocatalysis, cosmeceutical, ferulic acid, starch-oil composites, sunscreen

SOY-BASED BIOSOLVENTS: A REAL ALTERNATIVE TO VOC-GENERATING INDUSTRIAL SOLVENTS

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Key words : biosolvents, fatty acid methyl esters, surface cleaning, epoxy resin pre-polymers, co-solvent of supercritical CO_2

Since the 1990s, more and more constraining environmental regulations have been voted to fight against pollution caused by solvents.

National efforts to reduce air pollution in the United States have been intensified by the 1990 amendments to the Clean Air Act.

At the European level, two directives have been established with the target to reduce VOCs (Volatile Organic Compounds) emissions in the atmosphere. Directive 99/13/CE concerns the emissions from industrial equipments and Directive 2004/42/CE concerns the content of VOCs from solvent used to dilute architectural paints and varnishes and car refinishing paints. Moreover, in the European Union, the REACH Regulation adopted on December 2006 confers greater responsibility to industry to manage the risks from chemicals and to provide safety information on the substances.

As a consequence, biosolvents have highly attracted the attention as an alternative to many conventional chlorinated, fluorocarbon and petroleum industrial solvents, responsible of VOC emission and greenhouse gas production [1,2].

Among substitution solvents used until now, the methyl ester derived from different vegetable oils are very interesting due to their high biodegradability, low toxicity, low vapor pressure and non-inflammability. Methyl soyate is currently used in America and it is not classified by the US Environmental Protection Agency as a Hazardous Air Pollutant (HAP), nor an Ozone Depleting Chemical (ODC), nor a volatile organic compound. The characteristics of methyl soyate are given in Table 1 and its fatty acid methyl esters (FAME) composition in Table 2.

Property	Value	Reference
Density	0.874 g/cm^3	ASTM D1298
Boiling point	> 400°F	ASTM D 2887
Vapor pressure	< 0.1 mmHg	ASTM D 5191
Evaporation rate	0.0098	ASTM 3539
VOCs	< 50g/mL	ASTM 3960
Flash point	> 360° F	ASTM 455
Kauri-butanol value	58	ASTM D1133
Theoretical Hansen Parameters	δd=15.9 ; δp=1.5 ; δh=4.5 MPa ½	[3]
Experimental Hansen Parameters	δd=16.6 ; δp=5.2 ; δh=8.2 MPa ½ solubility sphere radius=9.5 MPa ½	[3] – test of solubility with 60 solvents

Table 1. Properties of methyl soyate

Fatty acid	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Arachidic C20:0	Gadoleic C20:1
%(w/w)	10.8	3.8	24.1	52.6	5.5	0.4	0.3

Table 2: Fatty acid profile of methyl soyate (Cognis France)

Methyl soyate is competitive as an industrial solvent because its cost does not rise beyond that of most of petrochemical solvents, creating additional market opportunity for soy-based products.

These remarkable characteristics encourage the study of its performances as alternative solvents in numerous applications [4, 5]. Among them, we can outline :

Ink formulations :

Methyl soyate has been used in newspaper inks in the United States since 1987 replacing conventional petrochemical carriers. As defined by the ink industry, it acts as a carrier solvent, diluent or binder for pigments to the substrate [6].

Agrochemical adjuvant :

Methyl soyate replaces also mineral oil as agrochemical adjuvant in some pesticides formulations, improving effectiveness, applicator safety, spread ability and environmental impact. Some adjuvants for agricultural chemicals are microemulsions made from all components naturally derived and readily biodegradable [7-9].

Bituminous flux

Vegetable oil methyl esters are used as fluxes for bitumen because of their ability to thin these binders. They substitute petroleum or carbochemical derivatives to reduce emission of fumes and VOCs and to work below the flash point of the resulting binder [10].

Cleaning solvent

Up to now, methyl soyate is essentially used as a biosolvent in many industrial cleaning applications [12-14] like screen printing ink cleaners, paint strippers, graffiti removers, asphalt cleaners, metal degreasers, oil spill clean-up, adhesive removers , safe household cleaners and hand cleaners [12]. However methyl soyate is generally formulated with cosolvents and/or surfactants to accelerate drying or water rinsing. Indeed, the slow evaporation of methyl soyate, resulting in a greasy film residue, limits some of the uses such as precision cleaning and electronics applications because they require pollutant-free material for printed boards and other contamination-sensitive parts.

Aim of this work : solvent for epoxy resin pre-polymers

In order to continue to expand the solvent market for the methyl soyate and other similar fatty acid methyl esters (FAME), we studied their performances as alternative solvents for epoxy resins pre-polymers: bisphenol A diglycidyl ether (DGEBA) and triglycidyl p-aminophenol ether (TGPA), depicted on figure 1. Indeed, these compounds are widely used in the industry as basic monomers for the production of two major polymers: epoxy resins and polycarbonates, which are used in several industrial sectors such as petrochemical and energy fields, packaging, restoring, panels and composites, adhesives… These applications involves the cleaning of manufacturing and conditioning materials by using the common solvents like methyl ethyl ketone and acetone.

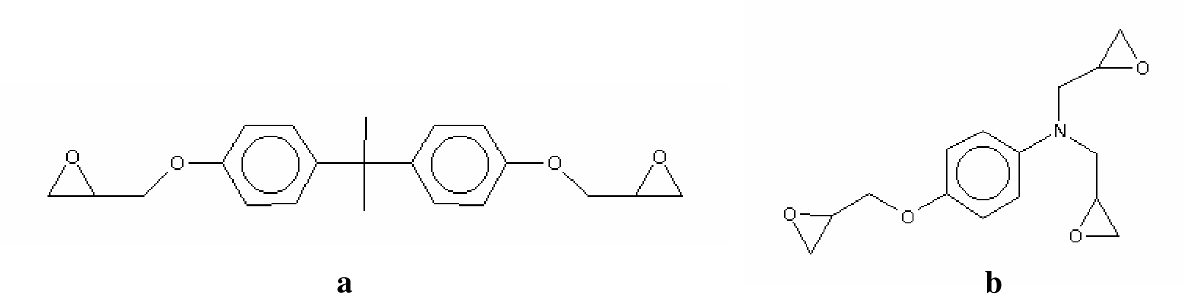

Figure 1. **a)** Bisphenol A diglycidyl ether (DGBA), **b)** Triglycidyl p-aminophenol ether (TGPA)

The methodology used involves the determination of FAME physical and chemical properties like Hansen parameters, viscosity, binary diffusion coefficient and vaporization enthalpy to explain their solubility performances. These parameters are important to evaluate the potential as solvent of any FAME including methyl soyate.

Concentrations measured on saturated solutions of the two prepolymers in FAME are presented in Table 3. These results show that concentrations at the saturation point decrease as the hydrocarbon chain length increases. Only methyl oleate showed an atypical behavior due to the specific interactions conferred by the mono-insaturation.

	Methyl Caprylate (C8)	**Methyl Laurate (C12)**	**Methyl Myristate (C14)**	**Methyl Oleate (C18:1)**	**Methyl Linoleate (C18:2)**
DGEBA	0.58	0.20	0.08	0.14	0.05
TGPA	0.57	0.10	0.04	0.08	0.06

Table 3. Concentrations of Bisphenol A diglycidyl ether (DGEBA) and Triglycidyl p-aminophenol ether (TGPA) in fatty acid methyl ester saturated solutions at 20°C (Values in g/ml +/-0.004).

In order to explain the solvency performances observed, Hansen solubility parameters [3] of epoxy resin pre-polymers and of fatty acid methyl esters C:8 to C:18 were first calculated theoretically then determined experimentally (Table 1). The first parameter, δd, is related to dispersion forces, the second one, δp, to polar forces, and the last one δh to specific interaction forces (hydrogen bonding, acid/base interactions, etc.). FAME Hansen parameters determined by experimentation showed no noticeable variation with the augmentation of hydrocarbon chain length. Nevertheless, Hansen parameters determined by group contribution [16] are shown to be capable of taking into consideration the hydrocarbon chain length contributions through the polarizability and the dipole moment.

It was found that the distance between FAME and pre-polymer solubility sphere centres (coordinates : Hansen parameters) can be correlated to the solubility limits for the selected FAME serie. For both resins, solubilization decreases as the distance between the solubility sphere centres rises.

Solubilization of DGEBA and TGPA was shown to depend on solvent vaporization enthalpy, FAME kinematic viscosity and binary diffusion coefficient, which are properties representative of the cohesion energy between solvent molecules, and momentum and mass transport respectively. Complete solubilization observed for DGEBA and TGPA in methyl caprylate as solvent, is probably due to the favourable conditions of mass and momentum transport and solvent-solvent molecules interactions. Decrement of solubility rates according to the methyl ester hydrocarbon chain length increment can be explained, on the one hand, by the steric hindrance of long molecules which makes difficult the motion of solvent molecules from the bulk to the pre-polymer surface where solubilization takes place. On the other hand, strong solvent-solvent interactions penalize solvent-solute interactions resulting in a decrease of solubility.

DFT calculations have shown a greater dipolar moment for TGPA than for DGEBA and steric hindrance on TGPA molecule, which tend to confirm the highest solubility of DGEBA.

Obtained results and the properties of long chain vegetal esters have encouraged further research to improve the dissolution of both pre-polymers.

An association of FAME with supercritical carbon dioxide (sc-CO_2) seems to be an answer to compensate for the insufficient solubility for the cleaning of epoxy resin pre-polymer production or conditioning equipment parts [17]. When FAME were used as co-solvents of sc-CO_2, dissolution performance up to 99% was obtained in the cases of methyl caprylate, methyl oleate and methyl linoleate. The great influence of hydrocarbon chain lengths of fatty acid esters and their insaturation on the results can be explained by the lower intermolecular interactions between ester molecules, their liquid-vapor equilibrium and their diffusion properties. Thanks to its fatty acid profile, methyl soyate can be an adequate co-solvent of the supercritical CO_2.

Ultrasonic waves associated to the FAME solvent effect allow to improve the solubilization of both epoxy resin pre-polymers at industrial level. This can be explained by the generated mechanical action and the natural heating of the cleaning bath (until 45°C). This method has been adopted by the company DIMEX (France) to clean its conditioning equipment parts covered with epoxy resin pre-polymer. The biosolvent used in this case is pure sunflower oil methyl ester because of its lower price in Europe. But methyl soyate could be used advantageously in other countries.

Conclusion

This work shows that methyl soyate, which is constituted essentially of methyl linoleate and methyl oleate, is only partially efficient for cleaning solvent applications if it is used alone. In the particular case of epoxy resin pre-polymers, methyl soyate becomes an appropriate biosolvent when associated to ultrasonic waves or to supercritical CO_2. At present, we are developing other cleaning formulations on base of bioproducts including vegetable oil methyl ester for electronics applications.

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Transferência de Tecnologia, Lei de Inovação, e Parcerias entre o Setor Público e Privado no Brasil.

Embrapa

Transferência de Tecnologia

Rio de Janeiro, 12 de abril de 2007

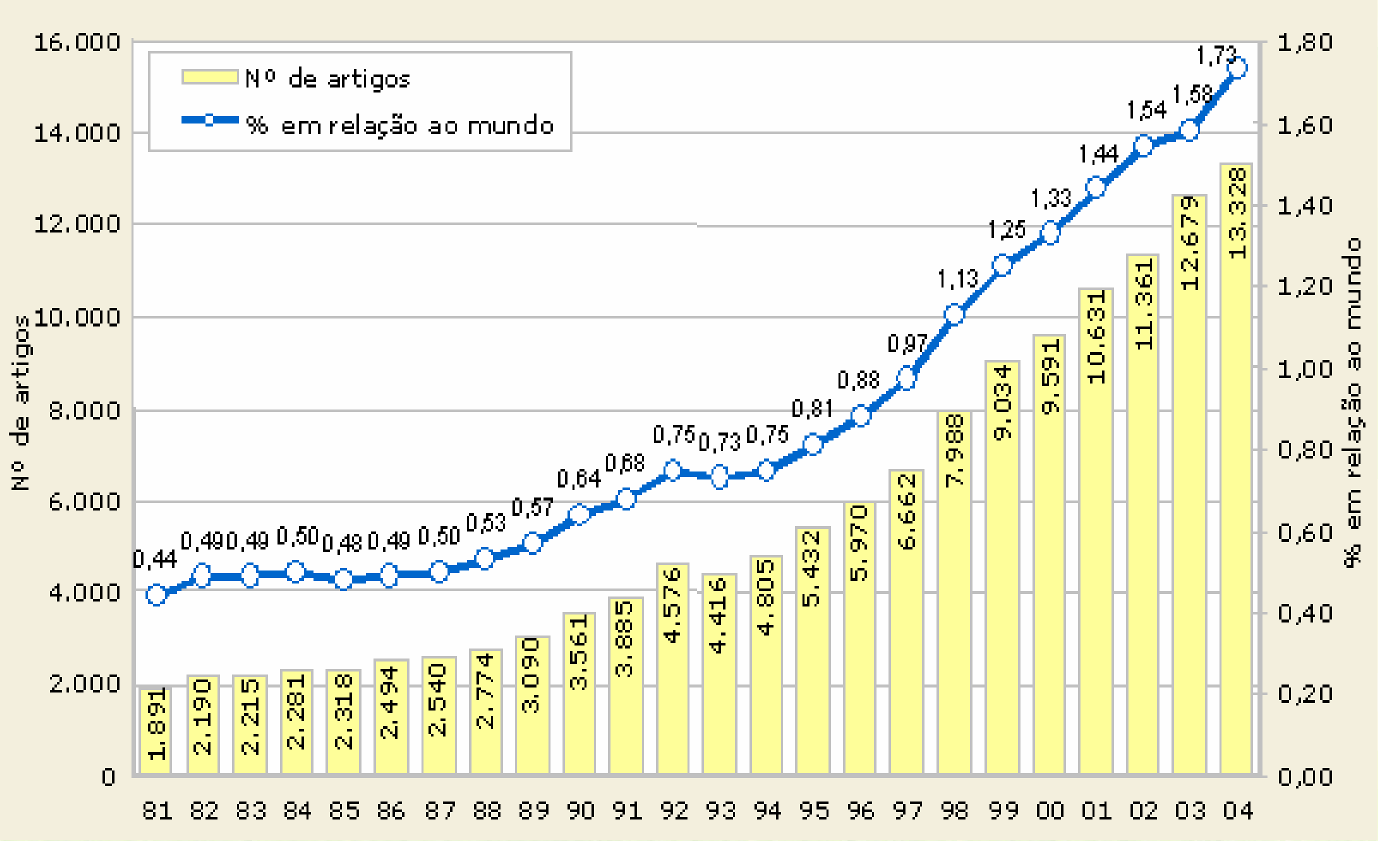
Pesquisa Científica e Tecnológica (Gênero)	*Inovação* (Espécie)
Foco na geração de conhecimento, seja teórico, abstrato, prático, inovador.	Foco no desenvolvimento de criações capazes de serem utilizados pelo mercado.
Investigação sistemática, incluindo o seu desenvolvimento, teste e avaliação, desenhada para desenvolver ou contribuir para a disseminação do conhecimento.	“Introdução de novidade ou aperfeiçoamento no ambiente produtivo ou social que resulte em novos produtos, processos ou serviços”

Pesquisa é transformar riqueza em conhecimento.
Inovação é transformar conhecimento em riqueza.

Fonte: Retirado de uma apresentação sobre inovação proferida pelo Dr. Paulo Crivinel

Pesquisa X Inovação

Pesquisa – Em 2004 o Brasil ocupava o 17º Lugar em Publicações Indexadas

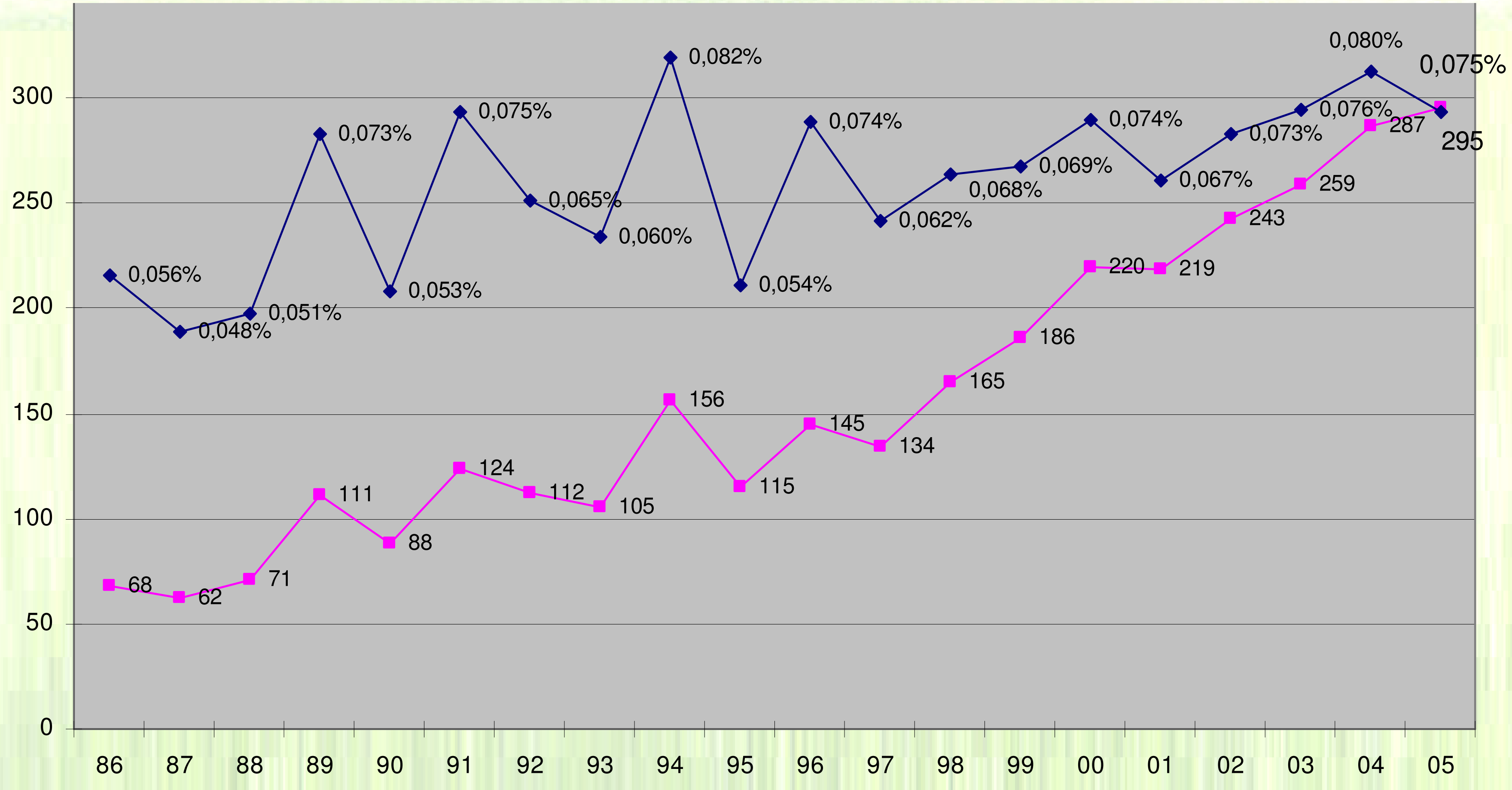


Área	*2002*	*2003*	*2004*
Ciências Agrárias	*3,00*	*3,36*	*3,34*

Fonte: Institute for Scientific Information (ISI). National Science Indicators.
Elaboração: Coordenação-Geral de Indicadores - Ministério da Ciência e Tecnologia.

Pesquisa X Inovação

Inovação – Em 2005 o Brasil ocupava o 31º Lugar em Depósitos de Patentes nos EUA



Fonte: USPTO / Patent Technology Monitoring Division (PTMD)

Relação entre Pesquisa e Inovação

Pesquisa Publicações em 2002	"Nº de Pesquisas que viraram Inovação"	*Inovação* Patentes no USPTO em 2002
Brasil - 11.285	**Brasil – 2%**	Brasil - 243
Índia - 17.325	**Índia – 5%**	Índia - 919
China - 33.561	**China – 5%**	China - 1.569
Coréia - 15.643	**Coréia – 51%**	Coréia – 7.937
Japão - 69.183	**Japão – 85%**	Japão – 58.739
Alemanha - 63.428	**Alemanha – 32%**	Alemanha – 20.418
USA - 245.578	**USA – 72%**	USA – 177.511

Brasil
1980 - 53 patentes (US)
2003 - 259 patentes (US)
Profissionais em C&T
89 % nas ICT
11 % nas empresas
Investimento em P,D&I
ICT – 60,2% X 39,1% Empresas

Coréia
1980 - 33 patentes (US)
2003 – 10.411 patentes(US)
Profissionais em C&T
39% nas ICT
61% nas empresas
Investimento em P,D&I
ICT - 22,8% X 76,2% Empresas

Países	Anos	Governo	Empresas	Ensino superior	Privado sem fins lucrativos
Alemanha	2002	13,8	69,1	17,1	...
Argentina	2002	37,2	26,1	33,9	2,8
Austrália	2000	22,9	47,5	26,8	2,7
Brasil	2000	30,2	39,1	30,1	0,6
Canadá	2002	12,0	54,2	33,5	0,3
China	2002	28,7	61,2	10,1	...
Coréia	2001	12,4	76,2	10,4	1
Espanha	2001	15,9	52,4	30,9	0,8
Estados Unidos da América	2002	8,8	70,2	15,9	5,1
França	2002	16,9	62,2	19,5	1,4
Japão	2001	9,5	73,7	14,5	2,3
México	1999	45,0	25,5	26,3	3,1
Portugal	2002	19,8	34,5	35,6	10,2
Rússia	2002	24,5	69,9	5,4	0,2

Fonte: Organisation for Economic Co-operation and Development, Main Science and Technology Indicators, November 2003 e
Brasil: Sistema Integrado de Administração Financeira do Governo Federal (Siafi). Extração especial realizada pelo Serviço Federal de Processamento de Dados (Serpro) e Pesquisa Industrial de Inovação Tecnológica (Pintec) do Instituto Brasileiro de Geografia e Estatística (IBGE) - 2000.
Elaboração: Coordenação-Geral de Indicadores - Ministério da Ciência e Tecnologia.

Distribuição de pesquisadores em equivalência de tempo integral, por setores institucionais, de países selecionados, nos anos mais recentes disponíveis

Países	Anos	Setores		
		Governo	Empresas	Ensino superior
Alemanha	2001	14,6	59,7	25,7
Argentina	2002	37,6	11,3	49,3
Austrália	2000	13,6	24,4	59,8
Brasil	**2000**	**7,9**	**26,7**	**64,7**
Canadá	1999	8,2	54,5	36,6
China	2002	23,3	54,7	22,0
Coréia	2001	8,8	73,5	16,9
Espanha	2001	16,7	23,7	58,6
Estados Unidos da América	1999	3,8	80,5	14,7
França	2001	12,9	49,9	35,2
Itália	2000	21,7	39,5	38,9
Japão	2001	5,0	63,7	29,6
México	1999	34,5	16,2	48,7
Portugal	2001	20,6	15,4	50,4
Reino Unido	1998	9,1	57,9	31,1
Cingapura	2002	7,2	50,8	42,0
Rússia	2002	29,6	56,0	14,1

Fonte: Organisation for Economic Co-operation and Development, Main Science and Technology Indicators, November 2003 e Brasil: para empresas: Pesquisa Industrial de Inovação Tecnológica (Pintec) - 2000, do Instituto Brasileiro de Geografia e Estatística (IBGE); para estudantes de doutorado: Fundação Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes); e, para o restante: Diretório dos Grupos de Pesquisa no Brasil (DGP), Censo 2000, da Assessoria de Estatística e Informação (AEI), do Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

Elaboração: Coordenação-Geral de Indicadores - Ministério da Ciência e Tecnologia.

Notas: Pesquisadores em equivalência de tempo integral: neste no cálculo, e no caso do Brasil, consideram-se as hipóteses: os pesquisadores das instituições de ensino superior e os estudantes de mestrado e doutorado que pertencem a grupos de pesquisa, dedicam 50% de seu tempo às atividades de pesquisa. Os pesquisadores dos institutos de pesquisa e do setor privado sem fins de lucro, dedicam 100%. No caso dos pesquisadores em empresas, considerou-se a dedicação informada à Pintec.

Lei nº 10.973, de 02.12.2004

Dispõe sobre incentivos à inovação e à pesquisa científica e tecnológica no ambiente produtivo e dá outras providências.

I - DISPOSIÇÕES PRELIMINARES
II - **DO ESTÍMULO À CONSTRUÇÃO DE AMBIENTES ESPECIALIZADOS E COOPERATIVOS DE INOVAÇÃO**
III - **DO ESTÍMULO À PARTICIPAÇÃO DAS ICT NO PROCESSO DE INOVAÇÃO**
IV - **DO ESTÍMULO À INOVAÇÃO NAS EMPRESAS**
V - DO ESTÍMULO AO INVENTOR INDEPENDENTE
VI - DOS FUNDOS DE INVESTIMENTO
VII - DISPOSIÇÕES FINAIS

Estímulo à construção de ambientes especializados e cooperativos de inovação

- Apoio à constituição de alianças estratégicas e o desenvolvimento de projetos de cooperação;

- Permissão para a ICT compartilhar seus laboratórios, equipamentos, instrumentos, materiais e demais instalações (incubação e pesquisa);

- Participação de ICT do capital de empresa privada de propósito específico (EPE).

Estímulo à participação das ICT no processo de inovação

- Simplificação para a celebração de contratos de transferência de tecnologia e de licenciamento (Inexigibilidade de Licitação);
- Estímulo à celebração de contratos de prestação de serviços e acordos de parceria;
- Possibilidade de recebimento de bolsa pelos pesquisadores envolvidos nos contratos acima;
- Divisão entre as equipes de pesquisa de até 1/3 dos ganhos econômicos auferidos pela ICT na exploração econômica de suas tecnologias;

Estímulo à participação das ICT no processo de inovação

- Vedação ao dirigente, ao criador ou a qualquer servidor, militar, empregado ou prestador de serviços de ICT divulgar, noticiar ou publicar qualquer aspecto de criações sem antes obter expressa autorização da ICT. (Operacionalização)

- Possibilidade de afastamento de pesquisador para prestar colaboração à outra ICT;

- Possibilidade de concessão ao pesquisador de licença sem remuneração para constituir empresa com a finalidade de desenvolver atividade empresarial relativa à inovação;

- Obrigatoriedade de manutenção nas ICT de um núcleo de inovação tecnológica.

Estímulo à inovação nas empresas

- Concessão de recursos financeiros, humanos, materiais ou de infra-estrutura diretamente às empresas privadas para a realização de P,D&I;
- Permissão para a celebração de contratos de risco entre as ICT e empresas privadas;
- Permissão para se dar tratamento preferencial, na aquisição de bens e serviços pelo Poder Público, às empresas que invistam em pesquisa e no desenvolvimento de tecnologia no País;
- Incentivos fiscais para as empresas privadas.

Propriedade Intelectual

No Brasil, a entrada em vigor do Acordo sobre Aspectos dos Direitos de Propriedade Intelectual Relacionadas ao Comércio – TRIPS, acordo este vinculado à Organização Mundial do Comércio, a partir de 1995, levou à reformulação e/ou complementação da legislação nacional de proteção à Propriedade Intelectual, visando a adequá-la às novas regras sobre o assunto previstas naquele Acordo.

Deste modo, a partir de 1995, foram emanadas pelo Congresso Nacional uma série de normas para regular a proteção da Propriedade Intelectual no Brasil:

- Obras Literárias, Artísticas ou Científicas (Lei 9.610/98);
- Softwares (Lei 9.609/98);
- Produtos ou Processos Patenteáveis (Lei 9.279/96);
- Desenhos Industriais (Lei 9.279/96);
- Marcas (Lei 9.279/96);
- Indicações Geográficas (Lei 9.279/96);
- Cultivares (Lei 9.456/97).

O valor da PI

Exportações americanas cobertas por Proteção Intelectual

Em 1947 - menos de 10%;
Em 1986 - 37%.
Em 1994 - mais de 50%

Valor da Marca

American Express - 81% do seu valor patrimonial
Kellogs - 94% do seu valor patrimonial
Coca-Cola - 95% do seu valor patrimonial
Microsoft - o valor dos ativos intangíveis é 12 vezes maior do que o dos ativos tangíveis
Banespa - U$ 500 milhões pelos tangíveis e U$ 3 bilhões pela marca (pago pelo Banco Santander)
Jaguar - U$ 450 milhões pelos tangíveis e U$ 3 bilhões pela marca (pago pela Ford)
Rowntree - U$ 900 milhões pelos tangíveis e U$ 4,5 bilhões pela marca (pago pela Nestlé)
Kraft - U$ 3,2 bilhões pelos tangíveis e U$ 12,9 bilhões pela marca (pago pela Phillip Morris)

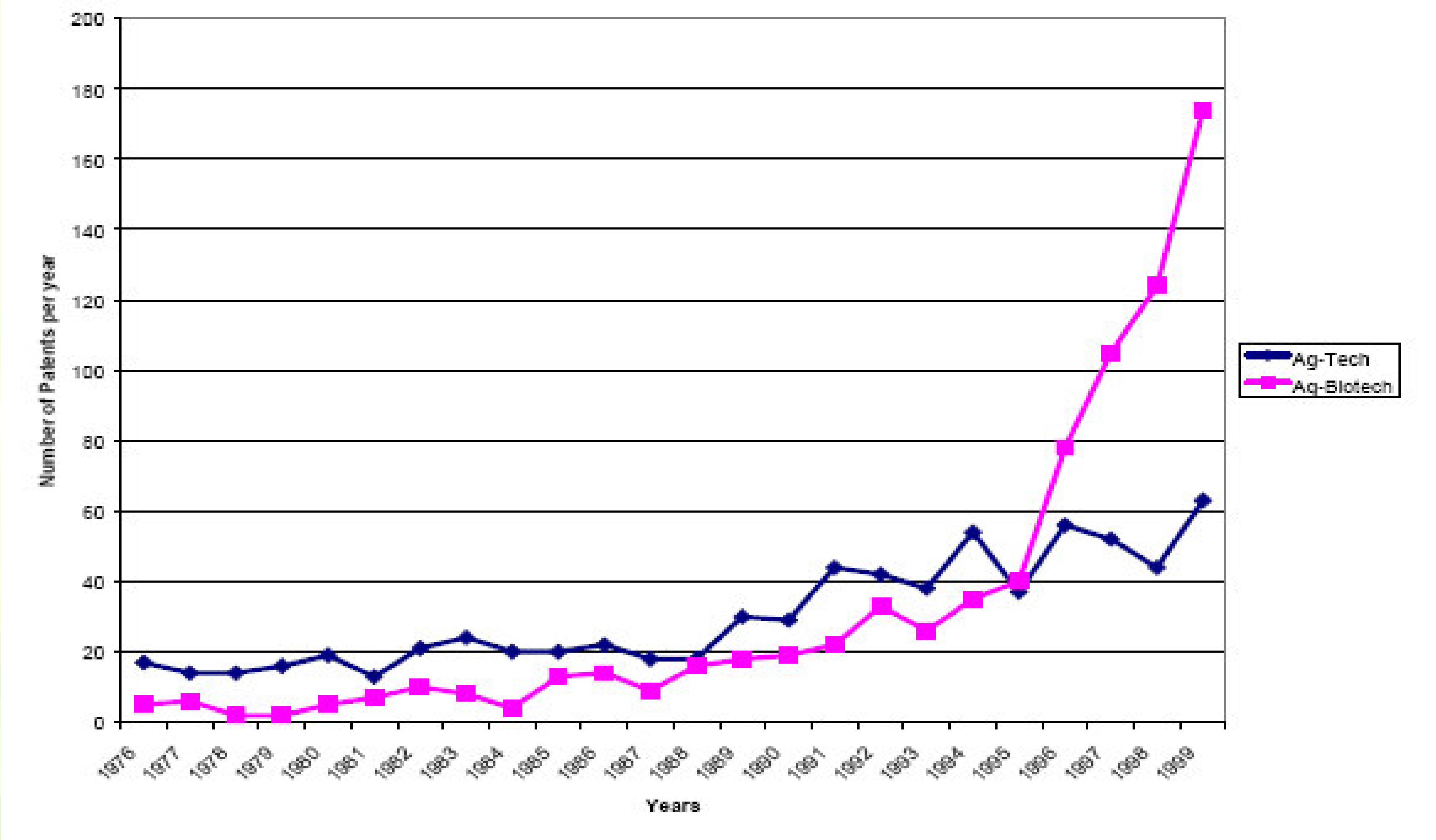
Valor da Informação

- Crescimento anual aproximado de 500 mil documentos de patentes no mundo;
- 71% da tecnologia tem divulgação exclusiva por patentes;
- Abrange todos os campos tecnológicos com estrutura uniforme;
- Contém a informação mais recente em relação ao estado da técnica;
- Disseminação do conhecimento pela descrição detalhada da invenção.

(Apresentação Sergio Barcelos – INPI, 12 de maio de 2006)

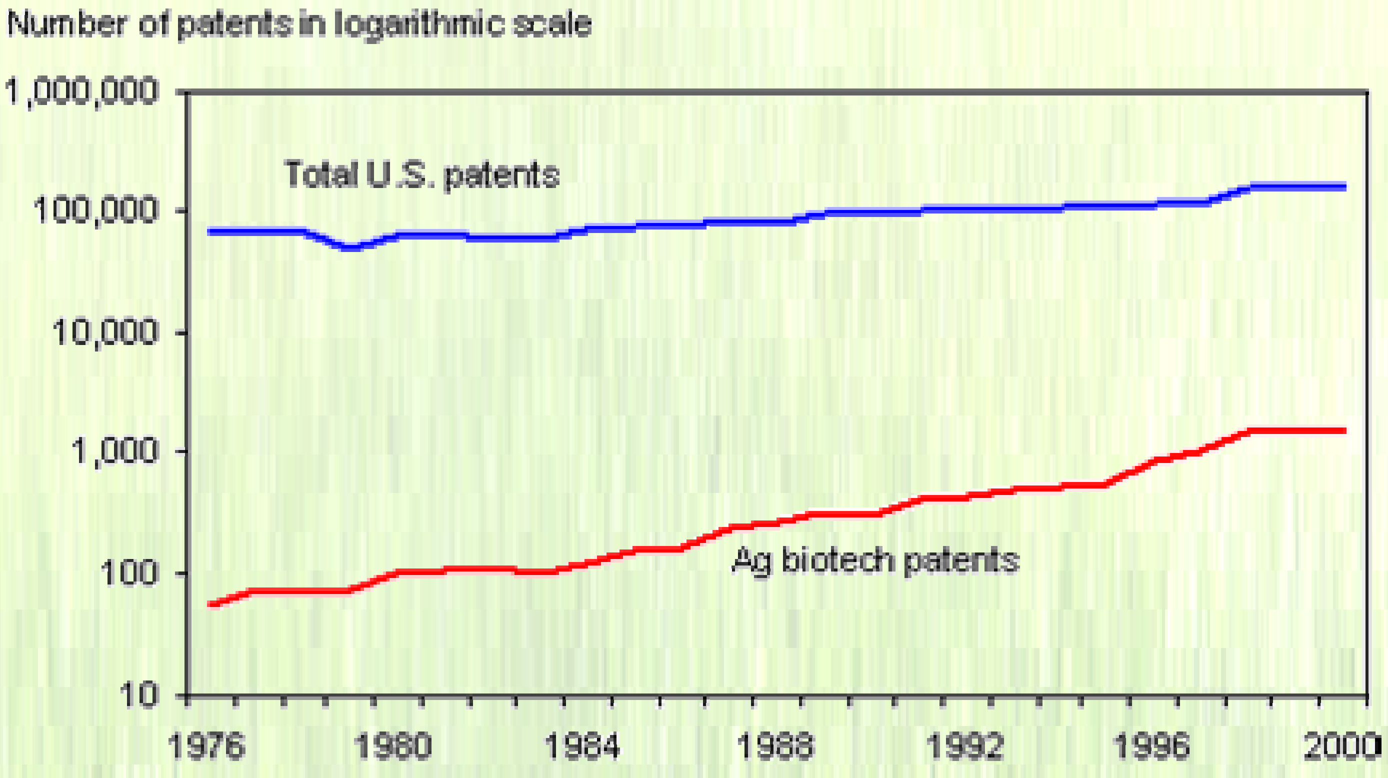
O risco de ser excluído do mercado

O Crescimento das Patentes em Biotecnologia Agrícola



O risco de ser excluído do mercado

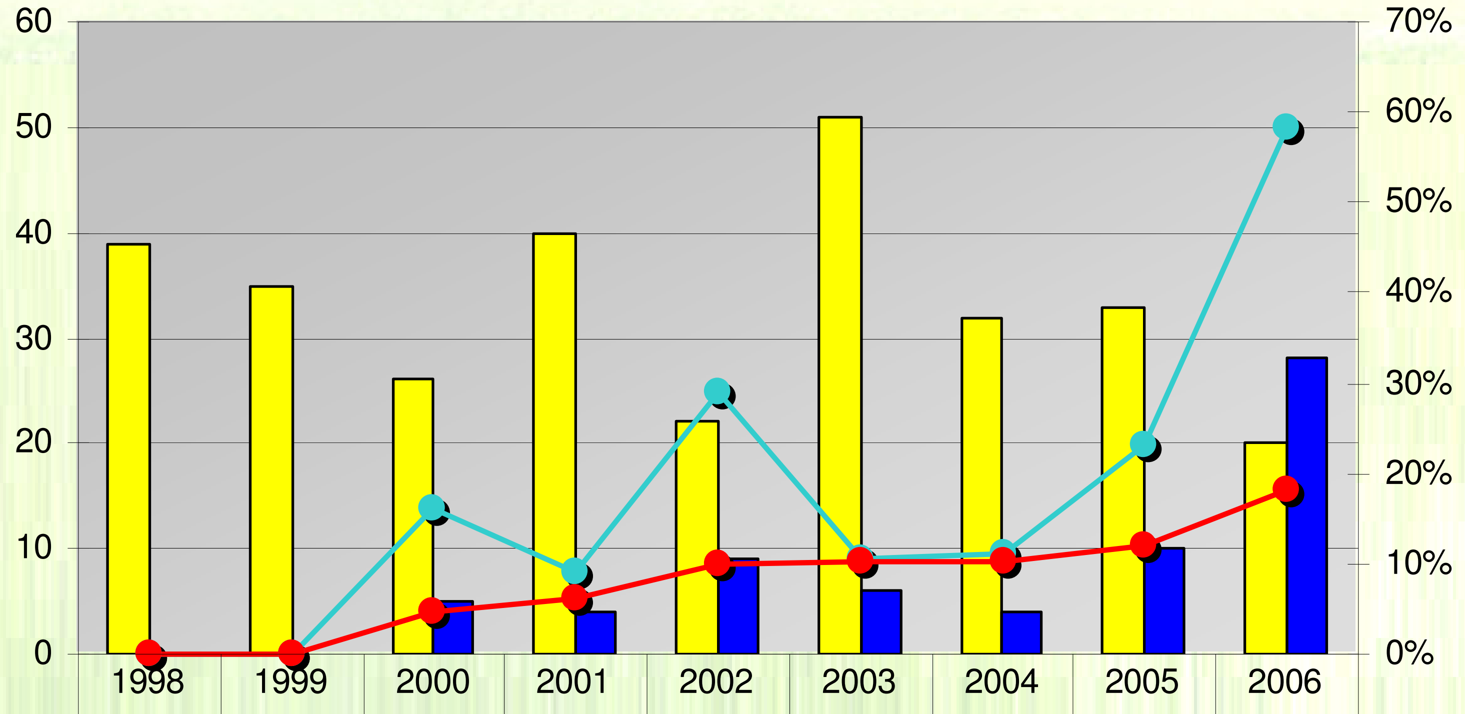
O Crescimento das Patentes em Biotecnologia Agrícola



Source: Based on data compiled from records of the U.S. Patent Office.

O risco de ser excluído do mercado

A Proteção da Soja Transgênica



	1998	1999	2000	2001	2002	2003	2004	2005	2006
🟨 Convencional	39	35	26	40	22	51	32	33	20
🟦 Transgênica	0	0	5	4	9	6	4	10	28
● Trans. no ano	0%	0%	16%	9%	29%	11%	11%	23%	58%
● Trans. acumulado	0%	0%	5%	6%	10%	10%	10%	12%	18%

Fonte: Filipe Teixeira – Embrapa Transferência de Tecnologia, Levantamento sobre a proteção de soja transgênica (RR) no Brasil, agosto de 2006 (dados do Serviço Nacional de Proteção de Cultivares – SNPC)

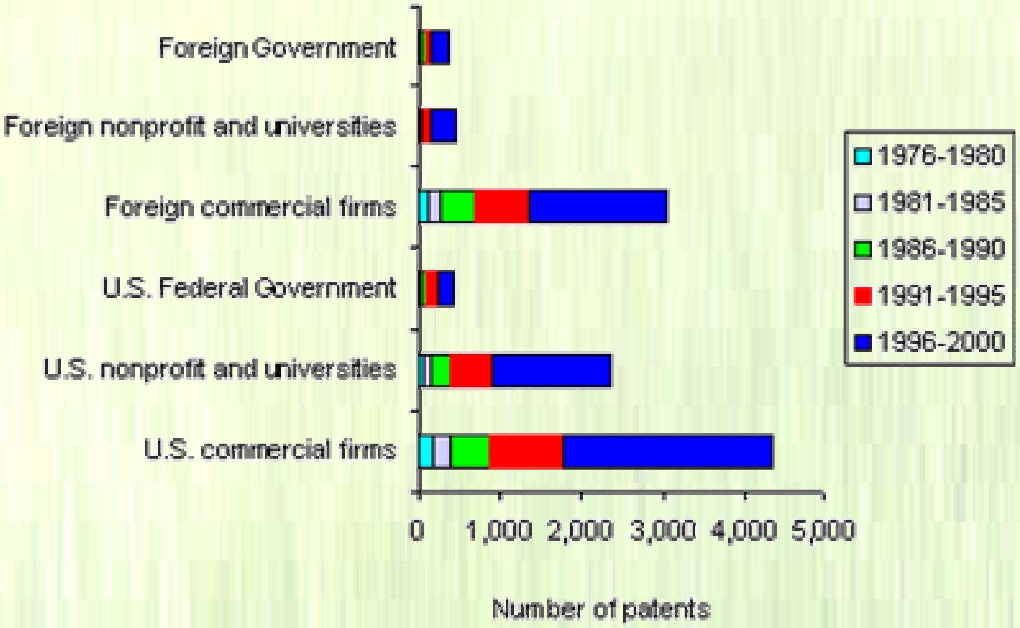
O risco de ser excluído do mercado

Biotecnologia e Transgenia

EUA/Brasil

No Brasil somente 27% dos depósitos de patente de invenção são feitos por residentes. (Fonte: INPI)

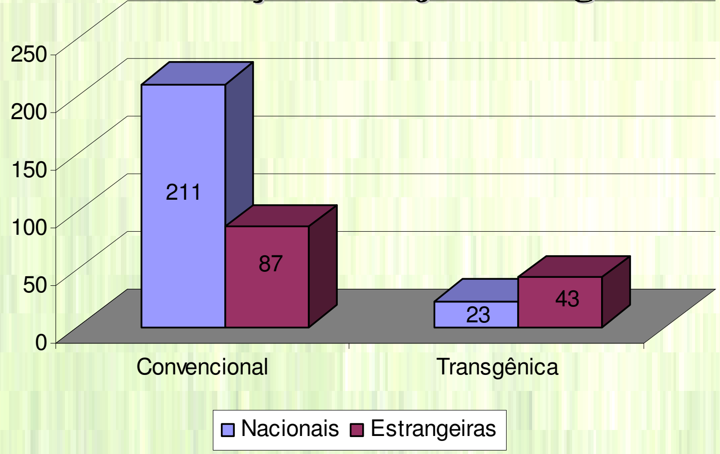
No campo da biotecnologia apenas 3% dos depósitos são de residentes no Brasil (Fortes, Maria Hercília Paim – INPI)



Source: Based on data compiled from records of the U.S. Patent Office.

Depósitos de Patente na Área da Biotecnologia Agrícola no USPTO

Proteção de Soja Transgênica



Fonte: Filipe Teixeira – Embrapa Transferência de Tecnologia, Levantamento sobre a proteção de soja transgênica (RR) no Brasil, agosto de 2006 (dados do Serviço Nacional de Proteção de Cultivares – SNPC)

Proteção de Tecnologias
Antes e depois da Instituição da Política de PI na Embrapa

		1977~1995	1996~2006	Total
Patentes	Brasil	72	118	190
	Ext.PCT	0	91	91
Marcas	Brasil	24	166	190
	Exterior	0	1	1
Softwares	Brasil	0	32	32
Cultivares	Brasil	0	276	276
	Exterior	0	19	19

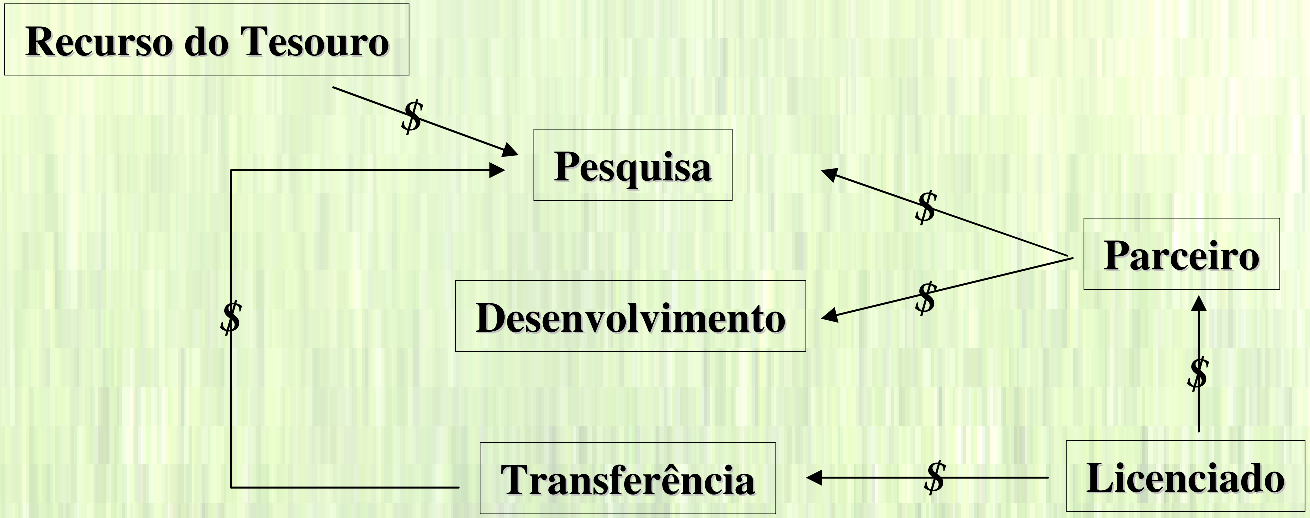
CONTRATOS DE PARCERIA

Lei de Inovação Tecnológica

Art. 9º

É facultado à ICT celebrar acordos de **parceria para realização de atividades conjuntas** de pesquisa científica e tecnológica e desenvolvimento de tecnologia, produto ou processo, com instituições públicas e privadas.

As partes deverão prever, em contrato, a **titularidade da propriedade intelectual** e a participação nos resultados da exploração das criações resultantes da parceria, **assegurando aos signatários o direito ao licenciamento**, observado o disposto nos §§ 4o e 5o do art. 6o desta Lei.



Recurso do Tesouro

Pesquisa

Parceiro

Desenvolvimento

Licenciado

Transferência

Exemplo de Parcerias para Inovação Tecnológica Desenvolvimento de Novas Cultivares de Soja

Em números

<u>- 22 Contratos de Parceria</u>

- –14 Contratos de Soja Convencional / 8 Contratos de Soja Transgênica (RR)

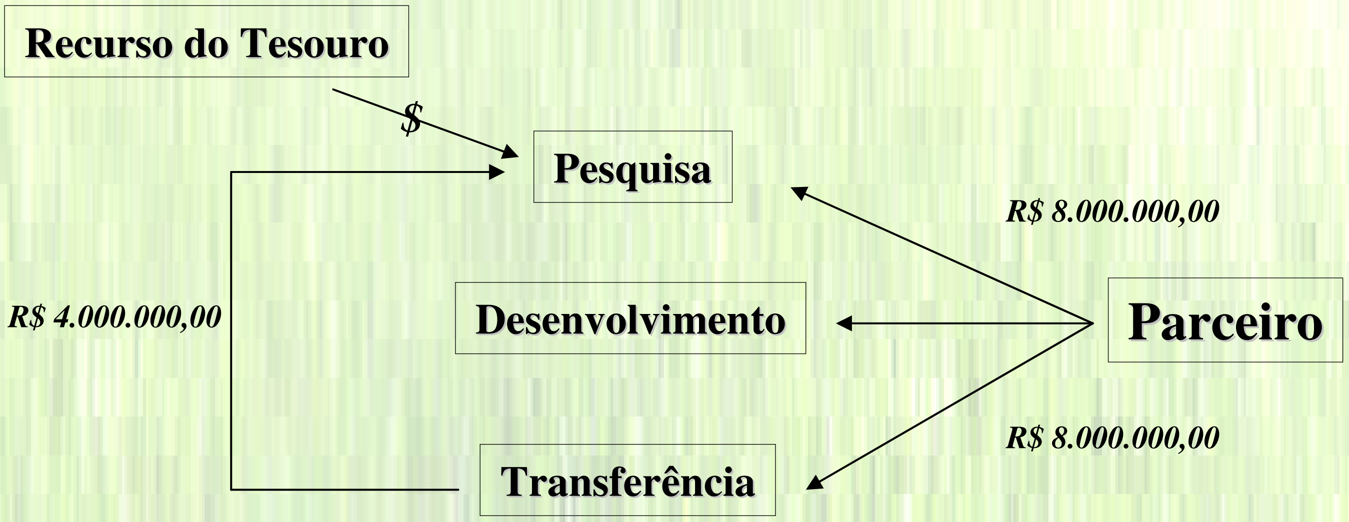
<u>- 10 Fundações:</u> CTPA, Meridional, Triângulo, Vegetal, FAPCEN, Bahia, Pró-Sementes, Cerrados, Centro Oeste e MT,.

<u>- 2 Empresas Estaduais de Pesquisa:</u> AGENCIARURAL e EPAMIG

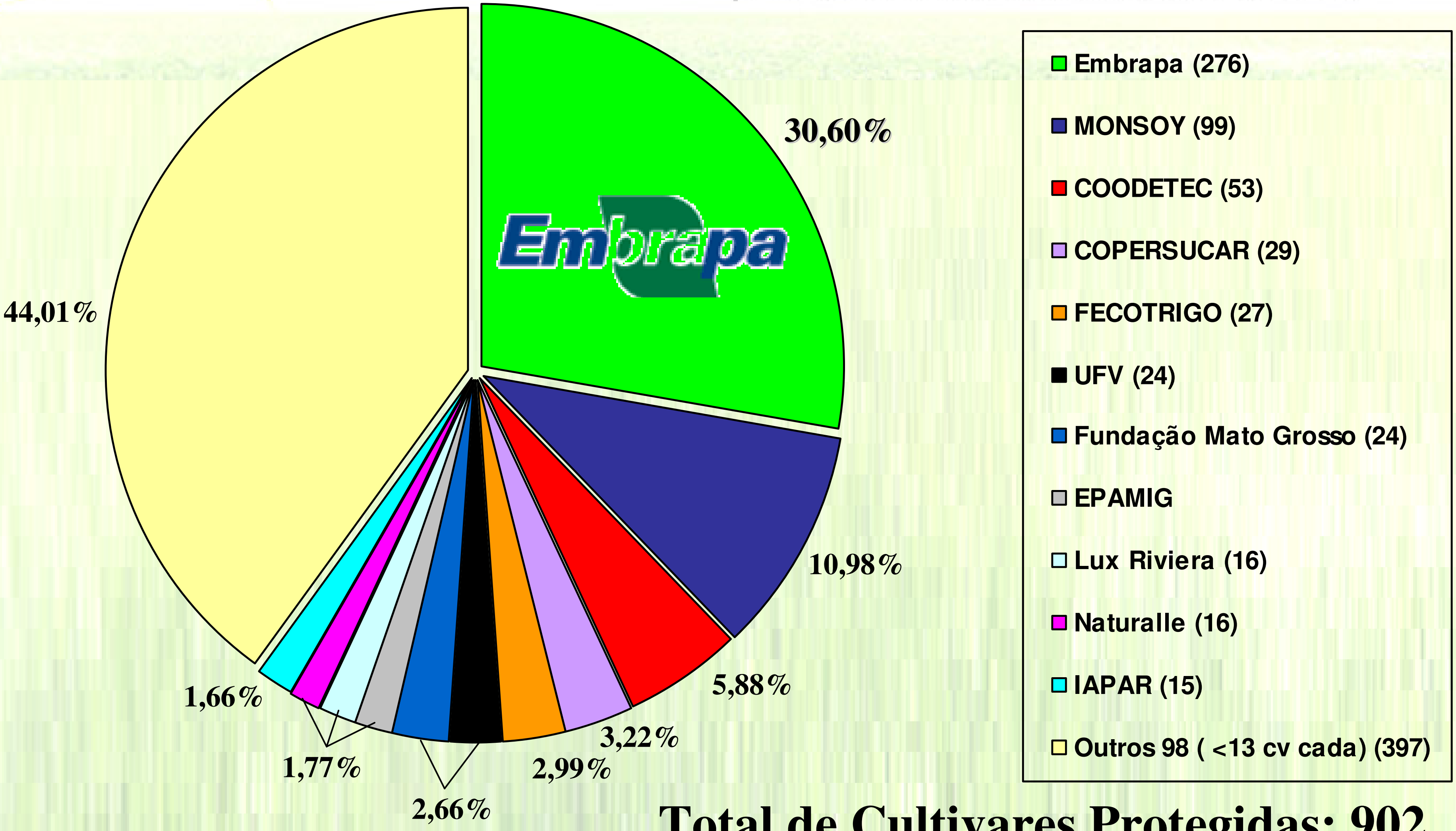
<u>- R$ 8 milhões (aproximadamente) Arrecadados com Royalties de Soja no Ano de 2006</u>

<u>- 93 Cultivares de Soja Protegidas até 2005</u>

<u>- + de 150 pontos de testes de novas cultivares de soja nas mais diversas condições edafoclimáticas brasileiras e em pelo menos outros 5 países da América Latina</u>



Participação das Cultivares da Embrapa no SNPC (em %)

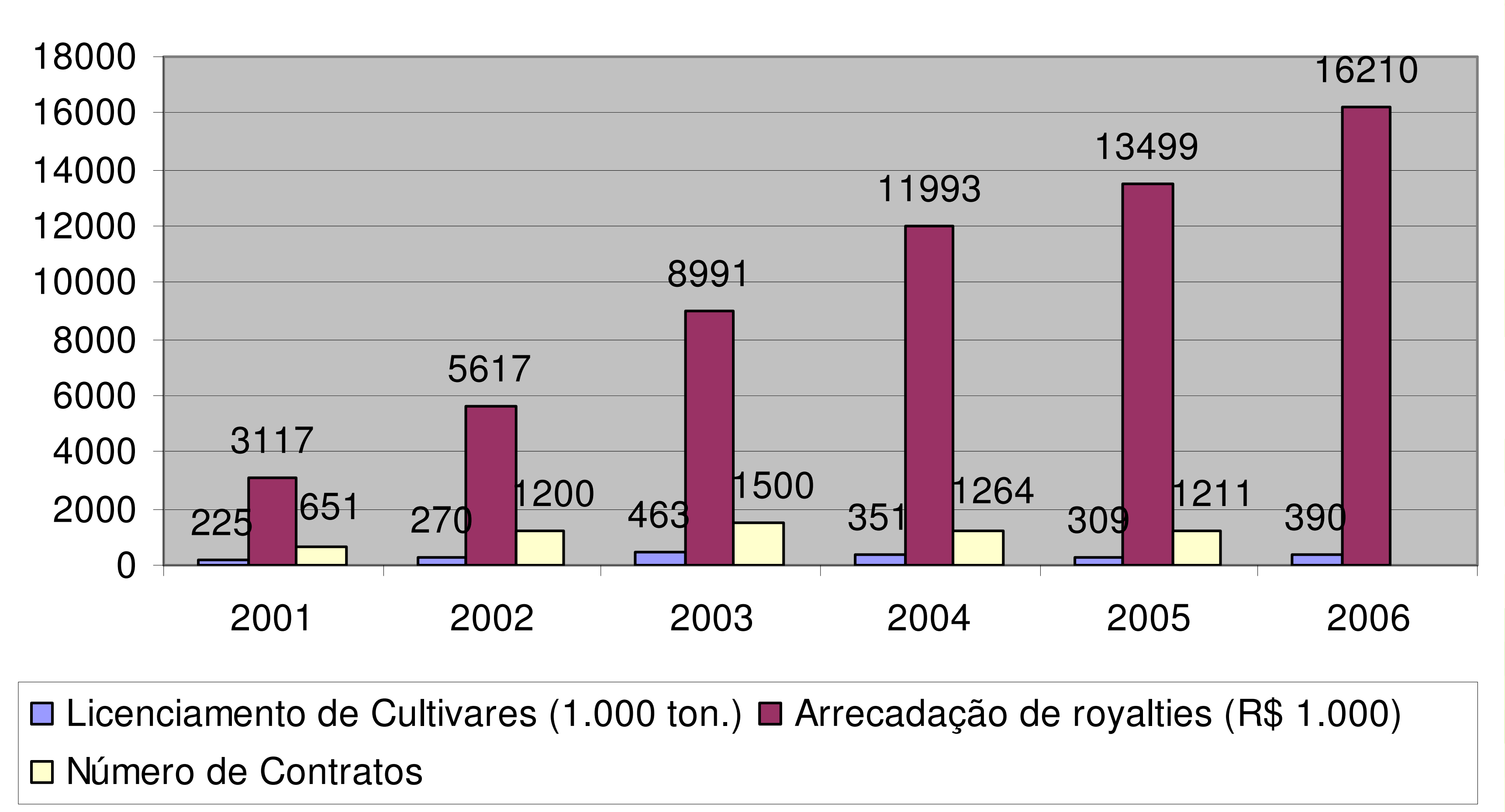


Total de Cultivares Protegidas: 902

Obs.: A soma dos percentuais por obtentor será maior que 100% em função da existência de cultivares protegidas em co-titularidade.

Fonte: Teixeira, Filipe – Levantamento da proteção de Cultivares no Brasil, Out./06

Royalties


18000
16000
14000
12000
10000
8000
6000
4000
2000
0
225
3117
651
270
5617
1200
463
8991
1500
351
11993
1264
309
13499
1211
390
16210
2001
2002
2003
2004
2005
2006
Licenciamento de Cultivares (1.000 ton.)
Arrecadação de royalties (R$ 1.000)
Número de Contratos

“Patenteamento e Transferência de Tecnologia no Setor Público”

“Uma explicação para que o setor público utilize o sistema de patentes é que o direito patentário não significa apenas o recebimento de royalties, mas também é um mecanismo pelo qual laboratórios públicos e outras instituições de pesquisa públicas podem transferir a tecnologia que eles desenvolveram de forma ampla.”

“As patentes nos institutos de pesquisa federais são tipicamente licenciadas para parceiros privados, dando-lhes incentivos para o subseqüente desenvolvimento comercial dos produtos.”

“A patente e o licenciamento devem ser consistentes com o objetivo de distribuir de forma ampla os benefícios das pesquisas geradas pelo ARS (“Serviço de Pesquisa Agropecuária”).”

“Os recursos advindos do licenciamento no ARS cobrem parcialmente as operações de seu Escritório de Transferência de Tecnologia (OTT) e só compõe 0.3 por cento do orçamento total da ARS.”

Government Patenting and Technology Transfer: By Paul W. Heisey, John L. King, Kelly Day Rubenstein, and Robbin Shoemaker
Economic Research Report No. (ERR15) 60 pp, March 2006 http://www.ers.usda.gov/Publications/ERR15/

"A melhor maneira de ter uma boa idéia é ter muitas idéias".
(Linus Pauling, químico americano, Prêmio Nobel de Química em 1954 e Nobel da Paz em 1962, 1901-1994)

Grato pela Atenção

Filipe Geraldo de M. Teixeira
Gerente de Propriedade Intelectual

Filipe.Teixeira@embrapa.br

Apresentação Não Disponível

Presentation Not Available