Ammonia, Hydrochloric Acid, Hydrogen Sulfide, N-hexane, Nitric Compounds, and Sulfuric Acid in the Food Processing Industry

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# Contents



# <span id="page-2-0"></span>Executive Summary

I searched Google, Google Scholar, Scopus, and AGRICOLA to compile the information included in these results. AP-42 was an excellent resource for determining which sectors of the industry used the chemicals about which you inquired.

I included some more general resources about the energy and environmental impact of the industry. In some cases, they included chapters relating to the information you're seeking. In others, they looked like they might contain useful background information about the industry and its processes.

I was unable to locate any journal articles about nitric compounds. From my research, it appears that these are mainly byproducts of animal feeding operations (i.e. manure). If you have more specific compounds in mind, please let me know and I'll do some more digging.

I was also unable to locate any articles relating to P2 practices relating to hydrogen sulfide. That also appears to be a byproduct of meat processing and is mainly a problem of odor control. I did find one article discussing biofiltration as an odor elimination option, for which I included the citation and abstract.

# <span id="page-3-0"></span>General information on P2/environmental practices in food

## processing

### AP-42: AP 42, Fifth Edition, Volume I Chapter 9: Food and Agricultural Industries

<http://www.epa.gov/ttnchie1/ap42/ch09/>

Provides detailed descriptions of the emissions from a variety of types of food processing operations.

### ENERGY STAR Focus on Energy Efficiency in Food Processing

[http://www.energystar.gov/buildings/facility-owners-and-managers/industrial-plants/measure](http://www.energystar.gov/buildings/facility-owners-and-managers/industrial-plants/measure-track-and-benchmark/energy-star-energy-4)[track-and-benchmark/energy-star-energy-4](http://www.energystar.gov/buildings/facility-owners-and-managers/industrial-plants/measure-track-and-benchmark/energy-star-energy-4)

### Energy Efficiency Improvement and Cost Saving Opportunities for the Fruit and Vegetable Processing Industry

[http://www.energystar.gov/buildings/tools-and-resources/energy-efficiency-improvement-and](http://www.energystar.gov/buildings/tools-and-resources/energy-efficiency-improvement-and-cost-saving-opportunities-fruit-and-vegetable)[cost-saving-opportunities-fruit-and-vegetable](http://www.energystar.gov/buildings/tools-and-resources/energy-efficiency-improvement-and-cost-saving-opportunities-fruit-and-vegetable)

### Energy Efficiency Improvement and Cost Saving Opportunities for the Baking

Industry [http://www.energystar.gov/buildings/tools-and-resources/energy-efficiency](http://www.energystar.gov/buildings/tools-and-resources/energy-efficiency-improvement-and-cost-saving-opportunities-baking-industry)[improvement-and-cost-saving-opportunities-baking-industry](http://www.energystar.gov/buildings/tools-and-resources/energy-efficiency-improvement-and-cost-saving-opportunities-baking-industry)

Fellows, P. J. (2009). *Food processing technology: Principles and practice.* Boca Raton : CRC Press. Find it in a library at [http://www.worldcat.org/oclc/845548920.](http://www.worldcat.org/oclc/845548920)

### Food Assessment Tool

#### [http://www.eng.utoledo.edu/aprg/ppis/pptools.htm#FAT](http://www.eng.utoledo.edu/aprg/ppis/pptools.htm%23FAT)

The Food Assessment Tool (FAT 1.0) is a self-assessment tool that provides technical support to food processing industry regarding the work practices to eliminate or reduce waste generation and determine using energy efficient methods. It focuses on questions related to several processes in a food industry. See the web site for a complete list. Developed by Ashok Kumar's team at the University of Toledo (contact information in the Expert Contacts section below)

Klemes, J., Smith, R., & Kim, J.-K. (2008). *Handbook of water and energy management in food processing*. Cambridge: Woodhead. Find it in a library at [http://www.worldcat.org/oclc/840439802.](http://www.worldcat.org/oclc/840439802)

Lung, Robert Bruce; Masanet, Eric; & McKane, Aimee. (2006). The Role of Emerging Technologies in Improving Energy Efficiency: Examples from the Food Processing Industry. *Lawrence Berkeley National Laboratory*. Lawrence Berkeley National Laboratory: Lawrence Berkeley National Laboratory. Retrieved from: [http://escholarship.org/uc/item/43c841xs.](http://escholarship.org/uc/item/43c841xs)

Mattsson, B., & Sonesson, U. (2003). *Environmentally-friendly food processing*. Boca Raton: CRC Press. Find it in a library at [http://www.worldcat.org/oclc/52566941.](http://www.worldcat.org/oclc/52566941)

In Sun, D.-W. (2014). *Emerging technologies for food processing*. Amsterdam : Academic Press. Find it in a library at [http://www.worldcat.org/oclc/888469581.](http://www.worldcat.org/oclc/888469581)

Wang, L. (2009). *Energy efficiency and management in food processing facilities*. Boca Raton: CRC Press. Find it in a library at [http://www.worldcat.org/oclc/154683825.](http://www.worldcat.org/oclc/154683825)

## <span id="page-4-0"></span>Peer reviewed journal articles

Hall, G. M., & Howe, J. (2012). Energy from waste and the food processing industry. *Process Safety and Environmental Protection*, 90(3), 203-212.

doi: <http://dx.doi.org/10.1016/j.psep.2011.09.005>

Abstract: The provision of a secure, continuous energy supply is becoming an issue for all sectors of society and the food processing industry as a major energy user must address these issues. This paper identifies anaerobic digestion as an opportunity to go some way to achieving energy security in a sustainable manner. However, a number of energy management and waste reduction concepts must also be brought into play if the environmental, social and economic aspects of sustainability are to be balanced. The reporting of such activity will help to promote the green credentials of the industry. Cleaner production, supply chain and life cycle assessment approaches all have a part to play as tools supporting a new vision for integrated energy and waste management. Our reliance on high-energy processing, such as canning and freezing/chill storage, might also need re-assessment together with processing based on hurdle technology. Finally, the concepts of energy and power management for a distributed energy generation system must be brought into the food processing industry.

Maxime, D., Marcotte, M., & Arcand, Y. (2006). Development of eco-efficiency indicators for the canadian food and beverage industry. *Journal of Cleaner Production*, 14(6–7), 636-648. doi: <http://dx.doi.org/10.1016/j.jclepro.2005.07.015> -- Includes a section on GHG emissions.

Abstract: Agriculture and Agri-Food Canada is developing eco-efficiency indicators (EEIs) in an effort to build a framework for a sustainable production system for the Canadian food and beverage industry (FBI). This paper presents the rationale and the framework of the project currently under development addressing the following environmental issues: energy use, emission of greenhouse gases, water use and wastewater generation, organic residues, and packaging residues. Proposed EEIs are intensity indicators and recycling ratios, and include environmental pressure modulators. They will be developed based on collected data and estimated impact levels, and reported by FBI sub-sector, geographical location, and establishment size. Objectives and methodologies are outlined. Problems on getting quality and reliable data on selected environmental issues are emphasized. The methodology will be published in 2005 and first results are due by 2008. Benchmarking and linkage to specific processing operations and management practices will help regulators and industries in promoting and implementing cleaner production initiatives and will lead to operational cost savings, product innovation, and enhanced competitiveness.

Panchev, I. N., Kirtchev, N. A., & Dimitrov, D. D. (2011). Possibilities for application of laser ablation in food technologies. Innovative Food Science & Emerging Technologies, 12(3), 369-374. doi: <http://dx.doi.org/10.1016/j.ifset.2011.02.008>

Abstract: This work considers the possibility for using laser ablation in food technologies. It was found for the fruits and vegetables under study that laser ablation provided an efficient peeling of the materials while preserving the organoleptic properties, such as freshness, naturalness, and texture. After a laser treatment of citrus fruit (oranges and lemons), the fruits were peeled and pectin was extracted from the peels via a classical type of extraction in HCl water solution. The pectins obtained were assayed for yield, degree of esterification, polyuronic content, molecular weight, gel strength and other physico-chemical properties. For all samples it was found that laser pretreatment of the materials led to an increase in pectin yield, gel strength and purity, at an insignificant reduction of molecular weight and degree of esterification. Laser ablation of fruits and vegetables was used as an alternative to traditional methods for producing edible films. The cell particles, removed by means of laser ablation and containing plant waxes, cellulose fibers and pectic substances, were applied aseptically onto a hard surface and the obtained edible films showed a lasting antimicrobial effect. As a result of the treatment of fruits and vegetables with CO2 laser, a number of aroma substances were released and they could be captured and used.

## <span id="page-5-0"></span>Expert contact Ashok Kumar, University of Toledo

akumar@utnet.utoledo.edu

# <span id="page-5-1"></span>Ammonia use in food processing and  $CO<sub>2</sub>$  as a refrigerant

## <span id="page-5-2"></span>General information

Ammonia and  $CO<sub>2</sub>$  are both replacements for CFC refrigerants. Below are some non-peer reviewed resources that provide some comparative information. Citations to peer-reviewed journal literature relating to  $CO<sub>2</sub>$  as an alternative are included in the next section. Ammonia is also emitted as a by-product of rendering operations in meat processing plants.

### ASHRAE Position Document on Ammonia as a Refrigerant

[http://www2.epa.gov/sites/production/files/documents/ASHRAE\\_PD\\_Ammonia\\_Refrigerant\\_20](http://www2.epa.gov/sites/production/files/documents/ASHRAE_PD_Ammonia_Refrigerant_2010_1.pdf) [10\\_1.pdf](http://www2.epa.gov/sites/production/files/documents/ASHRAE_PD_Ammonia_Refrigerant_2010_1.pdf)

### Longer Term Alternatives Refrigerants in the Caribbean

[http://www.pnuma.org/english/ozone/Documentos/GuyanaAC/Long%20Term%20Alternatives%](http://www.pnuma.org/english/ozone/Documentos/GuyanaAC/Long%20Term%20Alternatives%20Refrigerants,%20Henry%20Federicks,%20Grenada.pdf) [20Refrigerants,%20Henry%20Federicks,%20Grenada.pdf](http://www.pnuma.org/english/ozone/Documentos/GuyanaAC/Long%20Term%20Alternatives%20Refrigerants,%20Henry%20Federicks,%20Grenada.pdf)

This presentation compares the relative environmental benefits of ammonia, CO2, and several other refrigerants.

#### EPA Alternatives/SNAP > Refrigerants and Air Conditioning

<http://www.epa.gov/ozone/snap/refrigerants/index.html>

#### <span id="page-6-0"></span>Peer-reviewed journal articles

Cannaday, M. L., & Polycarpou, A. A. (2006). Advantages of CO2 compared to R410a refrigerant of tribologically tested aluminum 390-T6 surfaces. *Tribology Letters*, 21(3), 185-192. doi:<http://dx.doi.org/10.1007/s11249-005-9013-4>

Abstract: Carbon dioxide (CO2) is currently being investigated as a viable alternative refrigerant due to its environmental advantages. Much research is still needed regarding thermodynamic, tribological, and design issues, yet CO2 is a promising environmentally friendly refrigerant. This study investigates the physical and chemical changes of aluminum alloy disks that occur with increased severity tribotesting in the presence of either R410a or CO2 refrigerants while submerged in POE lubricant. Visibly and through surface profilometry, this study clearly shows that R410a environment results in increased disk wear compared to CO2 environment. In addition, Auger Electron Spectroscopy analysis was conducted showing that the oxygen concentration tends to increase with testing duration for both R410a and, to a greater extent, CO2 tested samples. When Auger data were compared for the R410a submerged in POE, CO2 submerged in PAG, and CO2 submerged in POE, the CO2 tested samples had significantly higher oxygen concentrations. This indicates that CO2 refrigerant is promoting a strong oxygenated layer, which reduces wear.

Cecchinato, L., Corradi, M., Fornasieri, E., & Zamboni, L. (2005). Carbon dioxide as refrigerant for tap water heat pumps: A comparison with the traditional solution. *International Journal of Refrigeration*, 28(8), 1250-1258. doi :<http://dx.doi.org/10.1016/j.ijrefrig.2005.05.019> Abstract: Increased concern about the environmental impact of the refrigeration technology is leading toward design solutions aimed at improving the energy efficiency of the related applications, using eco-friendly refrigerants, i.e. ozone-friendly and with the least possible global warming potential (GWP). In this respect, carbon dioxide (ASHRAE R744) is seen today as one of the most promising refrigerants and is raising great interest in industrial and scientific fields. In the present work, the plant options are investigated, which are related to the design of air/water heat pumps for tap water using CO2. A comparison is made, in terms of energy efficiency, between a system working with CO2 and a similar one working with HFC R134a; such a comparison is carried out by means of a simulation model of a refrigerating machine/heat pump, characterized by a detailed representation of the heat exchangers, based on their subdivision into elementary volumes. Results show that carbon dioxide is an interesting substitute for synthetic fluids, if the design of the system is focused to take advantage of its properties.

Pearson, A. (2005). Carbon dioxide—new uses for an old refrigerant. *International Journal of Refrigeration*, 28(8), 1140-1148. doi:<http://dx.doi.org/10.1016/j.ijrefrig.2005.09.005> Abstract: Carbon dioxide has been used as a refrigerant in vapour compression systems of many types for over 130 years, but it is only in the last decade that inventive minds and modern

techniques have found new ways to exploit the uniquely beneficial properties of this remarkable substance. This paper traces the development of the old carbon dioxide systems, considers the technical, commercial and social reasons for their slow development and subsequent decline and examines the recent renaissance across a surprisingly broad range of applications, from trans-critical car air conditioners to low temperature industrial freezer plants. The paper then concentrates on industrial refrigeration systems, which were the basis of early developments in the period 1865–1885, but which have been somewhat overlooked in the current renaissance. The paper concludes with a review of possible future developments, indicating the areas of research and product development required to maximise the potential of the only non-toxic, non-flammable, non-ozone-depleting, non-global-warming refrigerant available for Rankine cycle vapour compression systems in the 21st century.

Pereira, R. N., & Vicente, A. A. (2010). Environmental impact of novel thermal and non-thermal technologies in food processing. *Food Research International*, 43(7), 1936-1943. doi:<http://dx.doi.org/10.1016/j.foodres.2009.09.013>

Abstract: During the last 25 years, consumer demands for more convenient and varied food products have grown exponentially, together with the need for faster production rates, improved quality and extension in shelf life. These requests together with the severity of the traditional food processing technologies were driving forces for improvements in existing technologies and for the development of new food preservation technologies. Therefore, many technological developments have been directed towards unit operations such as pasteurization, sterilization, cooking and drying, and currently the new technological approaches for food preservation are serious candidates to replace the traditional well-established preservation processes. The aim of this review is to discuss the environmental impact that some of the most promising novel food preservation technologies may represent in terms of energy efficiency, water savings and reduced emissions. The emergence of novel thermal and non-thermal technologies allows producing high quality products with improvements in terms of heating efficiency and, consequently, in energy savings. Most of these technologies are locally clean processes and therefore appear to be more environment-friendly, having less environmental impact than the traditional ones. Novel processing technologies are increasingly attracting the attention of food processors once they can provide food products with improved quality and a reduced environmental footprint, while reducing processing costs and improving the addedvalue of the products.

# <span id="page-7-0"></span>Hydrochloric acid use in food processing

Hydrochloric acid may be used in food processing to:

• Regulate the pH level in a wide range of manufacturing and treatment processes including the production of drinking water, pharmaceuticals, beverages and foods;

- Process food additives including fructose, citric acid and hydrolyzed vegetable protein. See<http://www.codexalimentarius.net/gsfaonline/additives/details.html?id=178> for a complete list of the processes in which it is used as a food additive;
- As a solvent in the processing of shrimp waste;
- To wash blood and bone residue from meat carcasses in meat processing plants.

### <span id="page-8-0"></span>Peer-reviewed journal articles

Kandra, P., Challa, M., & Kalangi, P. J. (2012). Efficient use of shrimp waste: Present and future trends. *Applied Microbiology and Biotechnology*, 93(1), 17-29. doi: [http://dx.doi.org/10.1007/s00253-011-3651-2.](http://dx.doi.org/10.1007/s00253-011-3651-2)

Abstract: The production of shrimp waste from shrimp processing industries has undergone a dramatic increase in recent years. Continued production of this biomaterial without corresponding development of utilizing technology has resulted in waste collection, disposal, and pollution problems. Currently used chemical process releases toxic chemicals such as HCl, acetic acid, and NaOH into aquatic ecosystem as byproducts which will spoil the aquatic flora and fauna. Environmental protection regulations have become stricter. Now, there is a need to treat and utilize the waste in most efficient manner. The shrimp waste contains several bioactive compounds such as chitin, pigments, amino acids, and fatty acids. These bioactive compounds have a wide range of applications including medical, therapies, cosmetics, paper, pulp and textile industries, biotechnology, and food applications. This current review article present the utilization of shrimp waste as well as an alternative technology to replace hazardous chemical method that address the future trends in total utilization of shrimp waste for recovery of bioactive compounds.

# <span id="page-8-1"></span>N-hexane use in food processing

N-hexane is used:

- To remove oil from soybeans during vegetable oil processing. The resulting soybean oil and flakes are then desolventized to remove the hexane.
- In the flash desolventizing process to remove solvent from the drying process. Chapter 9.11.1-5 of AP-42 [\(http://www.epa.gov/ttnchie1/ap42/ch09/final/c9s11-1.pdf\)](http://www.epa.gov/ttnchie1/ap42/ch09/final/c9s11-1.pdf). The chapter is included in Appendix A of this report.

### <span id="page-8-2"></span>Peer-reviewed journal articles

Campbell, K. A., & Glatz, C. E. (2009). Mechanisms of aqueous extraction of soybean oil. Journal of Agricultural and Food Chemistry, 57(22), 10904-10912. Doi:<http://dx.doi.org/10.1021/jf902298a>

Abstract: Aqueous extraction processing (AEP) of soy Is a promising green alternative to hexane extraction processing. To improve AEP oil yields, experiments were conducted to probe the

mechanisms of oil release. Microscopy of extruded soy before and after extraction with and without protease indicated that unextracted oil is sequestered in an insoluble matrix of denatured protein and is released by proteolytic digestion of this matrix. In flour from flake, unextracted oil is contained as intact oil bodies in undisrupted cells, or as coalesced oil droplets too large to pass out of the disrupted cellular matrix. Our results suggest that emulsification is an important extraction mechanism that reduces the size of these droplets and increases yield. Protease and SDS were both successful in increasing extraction yields. We propose that this Is because they disrupt a viscoelastic protein film at the droplet interface, facilitating droplet disruption. An extraction model based on oil droplet coalescence and the formation of a viscoelastic film was able to fit kinetic extraction data well. ©2009 American Chemical Society.

Dunford, N. T. (2013). Technical advancements in pursuit of healthy and sustainable oils. Food Science and Technology (London), 27(2), 22-24.

Abstract: Recent advances that have had a significant impact on the nutritional and processing aspects of edible oils and oilseeds are discussed. Advancements in crop biotechnology, both traditional breeding and genetic engineering, allowed scientists to develop designer oilseeds tailored for specific applications. Improvements in fatty acid composition of seed oils targeted enhancements in nutritional or chemical properties to meet the needs and expectations of consumers and deliver functionality that is much needed by the food industry. Fractionation, hydrogenation, chemical inter esterification and blending of two or more oils have been used to deliver functional properties such as desirable melting, crystallization and flavor profiles and oxidative stability. Enzyme-aided aqueous oil extraction from oilseeds could be an attractive environmentally benign alternative to hexane extraction.

Jung, S., Maurer, D., & Johnson, L. A. (2009). Factors affecting emulsion stability and quality of oil recovered from enzyme-assisted aqueous extraction of soybeans. Bioresource Technology, 100(21), 5340-5347. DOI:<http://dx.doi.org/10.1016/j.biortech.2009.03.087>

Abstract: The objectives of the present study were to assess how the stability of the emulsion recovered from aqueous extraction processing of soybeans was affected by characteristics of the starting material and extraction and demulsification conditions. Adding endopeptidase Protex 6L during enzyme-assisted aqueous extraction processing (EAEP) of extruded soybean flakes was vital to obtaining emulsions that were easily demulsified with enzymes. Adding salt (up to 1.5 mM NaCl or MgCl 2) during extraction and storing extruded flakes before extraction at 4 and 30 °C for up to 3 months did not affect the stabilities of emulsions recovered from EAEP of soy flour, flakes and extruded flakes. After demulsification, highest free oil yield was obtained with EAEP of extruded flakes, followed by flour and then flakes. The same protease used for the extraction step was used to demulsify the EAEP cream emulsion from extruded full-fat soy flakes at concentrations ranging from 0.03% to 2.50% w/w, incubation times ranging from 2 to 90 min, and temperatures of 25, 50 or 65 °C. Highest free oil recoveries were achieved at high enzyme concentrations, mild temperatures, and short incubation times. Both the nature of enzyme (i.e., protease and phospholipase), added alone or as a cocktail, concentration of enzymes (0.5% vs.

2.5%) and incubation time (1 vs. 3 h), use during the extraction step, and nature of enzyme added for demulsifying affected free oil yield. The free oil recovered from EAEP of extruded flakes contained less phosphorus compared with conventional hexane-extracted oil. The present study identified conditions rendering the emulsion less stable, which is critical to increasing free oil yield recovered during EAEP of soybeans, an environmentally friendly alternative processing method to hexane extraction.

# <span id="page-10-0"></span>Hydrogen sulfide in food processing

Hydrogen sulfide is emitted:

- During the process of drying fish meal;
- During rendering operations in meat processing;
- As a by-product of the fermentation process when making distilled spirits.

## <span id="page-10-1"></span>Peer-reviewed journal articles

Shareefdeen, Z., Herner, B., & Wilson, S. (2002). Biofiltration of nuisance sulfur gaseous odors from a meat rendering plant. Journal of Chemical Technology and Biotechnology, 77(12), 1296- 1299. DOI:<http://dx.doi.org/10.1002/jctb.709>

Abstract: This paper presents a case study of a commercial biofilter, treating air streams contaminated with several odorous compounds including dimethyl sulfide, ammonia, methanethiol, hydrogen sulfide and ethylamine. The biofilter is packed with a proprietary woodbaed (BIOMIX™) medium which is designed to provide a good biological environment, pH buffer capacity, low pressure drop and resistance to compaction. This commercial biofilter treats a contaminated air volume of 15 000 actual cubic feet per minute (acfm) from a meat rendering and wastewater treatment operation with a 30-s empty bed residence time. The case study includes a novel gas sampling procedure and characterization of bipolar air streams through a mobile Fourier transform infrared system and olfactometer analysis. The results confirmed the good distribution of air, moisture and bacterial population across the medium. Four years of consistent performance of this commercial biofilter with >99% removal of 24500 odor units demonstrates that biofilters can be successfully applied for the removal of highly odorous gaseous sulfur compounds.

# <span id="page-10-2"></span>Nitric compounds in food processing

Nitric compounds are byproduct of animal feeding operations. According to *Air Emissions from Animal Feeding Operations: Current Knowledge, Future Needs* (National Research Council, 2002 [http://www.epa.gov/ttnchie1/ap42/ch09/related/nrcanimalfeed\\_dec2002.pdf\)](http://www.epa.gov/ttnchie1/ap42/ch09/related/nrcanimalfeed_dec2002.pdf), "An appreciable fraction of manure nitrogen is converted to NO by microbial action in soils and released into the atmosphere."

### <span id="page-11-0"></span>Peer-reviewed journal articles

I was unable to locate any journal articles related to P2 practices for these compounds

# <span id="page-11-1"></span>Sulfuric acid in food processing

Uses include:

- In the production of food acids (i.e. citric and lactic acids) and to directly control pH during processing, particularly of packaged foods and beverages, including seaweed extracts, alcoholic beverages, and cheeses.
- As a food additive to adjust the pH to create a more acidic environment that discourages the growth of bacteria and spoilage microbes. It's also used to adjust pH in the manufacture of cheeses and alcoholic beverages.
- As washes or sprays applied to the surface of meat and poultry products.

The Agricultural Marketing Services report on sulfuric acid [\(http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5101325\)](http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5101325) contains an excellent summary of its uses in the food processing industry.

### <span id="page-11-2"></span>Peer-reviewed journal articles

Gangagni Rao, A., Sasi Kanth Reddy, T., Vanajakshi, J., Joseph, J. & Sarma, P.N.. (2007). pH regulation of alkaline wastewater with carbon dioxide: A case study of treatment of brewery wastewater in UASB reactor coupled with absorber. *Bioresource technology*., 98, 2131-2136. doi: <http://dx.doi.org/10.1016/j.biortech.2006.08.011>

Abstract: Studies were carried out with carbon dioxide absorber (CA) to evaluate the usage of carbon dioxide (CO2) in the biogas as an acidifying agent by Up-flow Anaerobic Sludge Blanket (UASB) reactor. Investigation on the 5 l absorber revealed that ratio of brewery wastewater (BW) flow rate to biogas flow rate of 4.6-5.2 was optimum for minimum consumption of CO2 for acidification. The acidified BW after the absorber was treated in UASB reactor with optimum organic loading rate (OLR) of 23.1 kg COD/m3/day and hydraulic retention time (HRT) of 2 h. UASB reactor exhibited good performance with respect to reduction of chemical oxygen demand (COD) and methane yield. The implications of the present study on the full scale anaerobic reactor of medium scale brewery revealed that sufficient cost savings could be made if CO2 in the biogas or CO2 that was being wasted (let out to the atmosphere) can be used instead of sulfuric acid (H2SO4) for pH control.

#### **9.11.1 Vegetable Oil Processing**

#### 9.11.1.1 General<sup>1-5</sup>

The industry group producing fats and oils includes cottonseed oil mills, soybean oil mills, vegetable oil mills (other than corn, cottonseed, and soybean), and other mills. Wet corn mills are the primary producers of corn oil. Approximately 137 vegetable oil plants operate in the United States. Soybean processing, which dominates the industry, produces approximately 80 percent of the volume of vegetable oil and is concentrated in the states of Iowa, Illinois, Missouri, Kansas, Indiana, and Minnesota, but also found across the nation. Likewise, wet corn mills are concentrated in Corn Belt states. Cottonseed oil mills are found in southern states and California.

#### 9.11.1.2 Process Description $6-9$

The following process description discusses only soybean oil manufacture, because emission factors are available only for that activity. Corn, cottonseed, and peanut oil processing are similar to soybean processing, except for differences in the soybean preparation for oil extraction. The process for soybeans typically consists of five steps: oilseed handling/elevator operations, preparation of soybeans for solvent extraction, solvent extraction and oil desolventizing, flake desolventizing, and oil refining.

#### Oilseed Handling/Elevator Operations -

Figure 9.11.1-1 is a schematic diagram of a typical soybean handling/elevator operation that precedes the preparation of soybeans for the solvent extraction process.

Soybeans received at the facility by truck or rail are sampled and analyzed for moisture content, foreign matter, and damaged seeds. Then the beans are weighed and conveyed to large concrete silos or metal tanks for storage prior to processing. When the facility is ready to process the soybeans, the beans are removed from the silo or tank and cleaned of foreign materials and loose hulls. Screens typically are used to remove foreign materials such as sticks, stems, pods, tramp metal, sand, and dirt. An aspiration system is used to remove loose hulls from the soybeans; these hulls may be combined later with hulls from the dehulling aspiration step. The beans are passed through dryers to reduce their moisture content to approximately 10 to 11 percent by weight and then are conveyed to process bins for temporary storage and tempering for 1 to 5 days in order to facilitate dehulling.

#### Preparation Of Soybeans For Solvent Extraction -

Figure 9.11.1-2 is a schematic diagram of the process used to prepare soybeans for the solvent extraction process. The process, which is fairly well standardized, consists of four principal operations: cracking, dehulling/hull removal, conditioning, and flaking.

Soybeans are conveyed from the process bins to the mill by means of belts or mass flow conveyors and bucket elevators. In the mill, the beans may be aspirated again, weighed, cleaned of tramp metal by magnets, and fed into corrugated cracking rolls. The cracking rolls "crack" each bean into four to six particles, which are passed through aspirators to remove the hulls (processed separately after the removal of residual bean chips). These hulls may be combined with the hulls from the grain cleaning step.



Figure 9.11.1-1. Flow diagram of typical soybean handling/elevator operations. (Source Classification Codes in parentheses.)





Next, the cracked beans and bean chips are conveyed to the conditioning area, where they are put either into a rotary steam tubed device or into a stacked cooker and are heated to "condition" them (i. e., make them pliable and keep them hydrated). Conditioning is necessary to permit the flaking of the chips and to prevent their being broken into smaller particles. Finally, the heated, cracked beans are conveyed and fed to smooth, cylindrical rolls that press the particles into smooth "flakes", which vary in thickness from approximately 0.25 to 0.51 millimeters (0.010 to 0.020 inches). Flaking allows the soybean oil cells to be exposed and the oil to be more easily extracted.

#### Solvent Extraction and Oil Desolventizing -

The extraction process consists of "washing" the oil from the soybean flakes with hexane solvent in a countercurrent extractor. Then the solvent is evaporated (i. e., desolventized) from both the solvent/oil mixture (micella) and the solvent-laden, defatted flakes (see Figure 9.11.1-3). The oil is desolventized by exposing the solvent/oil mixture to steam (contact and noncontact). Then the solvent is condensed, separated from the steam condensate, and reused. Residual hexane not condensed is removed with mineral oil scrubbers. The desolventized oil, called "crude" soybean oil, is stored for further processing or loadout.

#### Desolventizing Flakes -

The flakes leaving the extractor contain up to 35 to 40 percent solvent and must be desolventized before use. Flakes are desolventized in one of two ways: either "conventional" desolventizing or specialty or "flash" desolventizing. The method used depends upon the end use of the flakes. Flakes that are flash desolventized are typically used for human foods, while conventionally desolventized flakes are used primarily in animal feeds.

Conventional desolventizing takes place in a desolventizer-toaster (DT), where both contact and noncontact steam are used to evaporate the hexane. In addition, the contact steam "toasts" the flakes, making them more usable for animal feeds. The desolventized and toasted flakes then pass to a dryer, where excess moisture is removed by heat, and then to a cooler, where ambient air is used to reduce the temperature of the dried flakes. The desolventized, defatted flakes are then ground for use as soybean meal (see Figure 9.11.1-4).

Flash desolventizing is a special process that accounts for less than 5 percent by volume of the annual nationwide soybean crush. The production of flakes for human consumption generally follows the flow diagram in Figure 9.11.1-3 for the "conventional" process, except for the desolventizing step. In this step, the flakes from the oil extraction step are "flash" desolventized in a vacuum with noncontact steam or superheated hexane. This step is followed by a final solvent stripping step using steam. Both the hexane vapor from the flash/vacuum desolventizer and the hexane and steam vapors from the stripper are directed to a condenser. From the condenser, hexane vapors pass to the mineral oil scrubber and the hexane-water condensate goes to the separator, as shown in Figure 9.11.1-3. The flakes produced by the flash process are termed "white flakes". A process flow diagram for the flash desolventizing portion of the soybean process is shown in Figure 9.11.1-5. From the stripper, the white flakes pass through a cooker (an optional step) and a cooler prior to further processing steps similar to the "conventional" process. A plant that uses specialty or "flash" desolventizing requires different equipment and is far less efficient in energy consumption and solvent recovery than a plant that uses conventional desolventizing. Given these facts, solvent emissions are considerably higher for a specialty desolventizing process than for a similar-sized conventional desolventizing process.



Soybean Extraction Facility--Total Hexane Losses (3-02-019-97) (3-02-019-98)

Figure 9.11.1-3. Flow diagram of the "conventional" solvent extraction process. (Source Classification Codes in parentheses.)



Figure 9.11.1-4. Flow diagram for "conventional" process of dry material sizing, grinding, and loadout. (Source Classification Codes in parentheses.)

9.11.1-6 EMISSION FACTORS 11/95



Figure 9.11.1-5. Flow diagram of the flash desolventizing process. (Source Classification Code in parentheses.)

Vegetable Oil Refining -

Crude oil is typically shipped for refining to establishments engaged in the production of edible vegetable oils, shortening, and margarine. Crude vegetable oils contain small amounts of naturally occurring materials such as proteinaceous material, free fatty acids, and phosphatides. Phosphatides are removed for lecithin recovery or to prepare the crude oil for export. The most common method of refining oil is by reacting it with an alkali solution which neutralizes the free fatty acids and reacts with the phosphatides. These reacted products and the proteinaceous materials are then removed by centrifuge. Following alkali refining, the oil is washed with water to remove residual soap, caused by saponification of small amounts of the triglycerides (oil). Color-producing substances within an oil (i. e., carotenoids, chlorophyll) are removed by a bleaching process, which employs the use of adsorbents such as acid-activated clays. Volatile components are removed by deodorization, which uses steam injection under a high vacuum and temperature. The refined oil is then filtered and stored until used or transported.

#### 9.11.1.3 Emissions And Controls $6,10-20$

#### Emissions -

Particulate matter and volatile organic compounds are the principal emissions from vegetable oil processing. Particulate matter (PM) results from the transfer, handling, and processing of raw seed. VOC emissions are the oil extraction solvent, hexane, which is classified as a hazardous air pollutant. Particulate emissions from grain handling are discussed in the Interim AP-42 Section 9.9.1, "Grain Elevators And Processes".

Solvent emissions arise from several sources within vegetable oil processing plants. There are potential solvent emissions from the transfer and storage of hexane on site as well as potential leaks from piping and vents. Small quantities of solvent (up to 0.2 percent by volume of oil) are present in the crude vegetable oil after the solvent is recovered by film evaporators and the distillation stripper. This hexane may volatilize during the oil-refining process; however, no emission data are available. Trace quantities of solvent are present and available for volatilization in waste water collected from the condensation of steam used in the distillation stripper and desolventizer-toaster. Emission data from waste water also are not available.

Vents are another source of emissions. Solvent is discharged from three vents: the main vent from the solvent recovery section, the vent from the meal dryer, and the vent from the meal cooler. The main vent receives gases from the oil extractor, the film evaporator and distillation stripper, and the desolventizer-toaster. Vents for the meal dryer and meal cooler typically vent to atmosphere.

#### Hexane Emissions -

The recommended method for estimating annual hexane emissions from soybean solvent extraction facilities is to obtain the annual hexane usage from the specific plant's records, and to assume that all hexane make-up is due to losses to the air (SCC 3-02-019-97). (Some hexane leaves the facilities as a small fraction of the oil or meal products, but this amount has not been quantified.) If the hexane usage is determined from purchase records and the purchased amount accounts for any change in quantities stored on-site, then storage tank losses would already be accounted for in the loss estimate. If the usage is determined from the amount metered out of the storage tanks, then the storage tank losses should be calculated separately, and in addition to, the usage losses, using the equations in AP-42 Chapter 7 or in the TANKS software. Careful application of such a material balance approach should produce emission estimates comparable in quality to those derived from a B-rated emission factor.

The mean total hexane loss reported by the plants in References 11 through 19 was 3.3 L/Mg (0.89 gal/ton [4.9 lb/ton]) of raw soybeans processed (SCC 3-02-019-98). This represents an overall total loss factor for soybean oil processing, encompassing all sources of vented and fugitive emissions (and storage tanks), as well as any hexane leaving the facility as part of the oil or meal products. For a new facility or if plant-specific usage data are unavailable, this factor, rated D, can be used as a default value until the relevant data for the facility become available. The default value should be used only until the facility can compile the data needed to develop a plant-specific hexane loss for the period of interest.

#### Particulate Emissions -

Table 9.11.1-1 presents emission factors for total PM emissions resulting from handling and processing soybeans in vegetable oil manufacturing. Emission factors are provided for PM-generating processes for the meal production process, including meal drying and cooling.

#### Table 9.11.1-1. TOTAL PARTICULATE EMISSION FACTORS FOR SOYBEAN MILLING<sup>a</sup>



#### EMISSION FACTOR RATING: E

<sup>a</sup> Emission factors are based on pounds per ton of soybeans processed by the unit. Factors represent controlled emissions, except as noted. Divide the lb/ton factor by two to obtain kg/Mg.  $SCC = Source Classification Code, ND = No Data.$ 

 $b$  Reference 21. These data were obtained from unpublished emission test data and from industry questionnaires. Because these are secondary data, the test data and the questionnaire results were weighed equally and the emission factors were calculated as arithmetic means of the data. The emission factor rating is a reflection of the source of the data.

 $\degree$  See Interim AP-42 Section 9.9.1, "Grain Elevators And Processes".

<sup>d</sup> Reference 22.

#### Controls -

Hexane is recovered and reused in the oil-extraction process because of its cost. The steam and hexane exhausts from the solvent extractor, desolventizer-toaster, and oil/hexane stripping are passed through condensers to recover hexane. Residual hexane from the condensers is captured by mineral oil scrubbers. The most efficient recovery or control device is a mineral oil scrubber (MOS), which is approximately 95 percent efficient. The meal dryer and cooler vents are typically exhausted to the atmosphere with only cyclone control to reduce particulate matter. Process controls to reduce breakdowns and leaks can be used effectively to reduce emissions. Quantities of hexane may be lost through storage tanks, leaks, shutdowns, or breakdowns. These losses are included in the material balance.

References for Section 9.11.1

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