# Utilization of almond residues

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**Abstract:** Almond production generates millions of tons of residues in addition to almond nuts. Almond residues, including shells, hulls, pruning, leaves, skin and inedible kernel disposition, are good feedstocks for production of bioenergy and other valuable compounds. In this article, research on the utilization of almond residues as energy and non-energy feedstocks is reviewed. Technical options for converting almond residues to energy and other valuable products are discussed. Several commercial conversion technologies are examined. Needs for further research and development are recommended.

**Keywords:** activated carbons, almond, anti-oxidants, bioenergy, biomass, biorefinery, gasification, heat, power, pyrolysis
**DOI:** 10.3965/j.issn.1934-6344.2010.04.001-018

**Citation:** Paul Chen, Yanling Cheng, Shaobo Deng, Xiangyang Lin, Guangwei Huang, Roger Ruan. Utilization of almond residues. Int J Agric & Biol Eng, 2010; 3(4): 1－18.

## 1 Introduction

Almond (*Prunus dulcis*) is a mid-size tree of rose family. Almond fruit consists of the hull, shell, and kernel (nut). The almond tree can grow to a height of seven to ten meters. The edible kernel or nut is separated and collected for commercial uses. The state of California in the US accounts for about 80% of the world's almond production on a shelled basis. For 2010 the California crop was forecasted to be about 740,000 metric tons (1,628 million pounds), which are accompanied by equal amount of shells, twice as much as hulls, and half as much as pruning (Figure 1). Other biomaterials may be generated from removal of old trees, tree branches and leaves collected during hulling, inedible kernel disposition from grading process, and almond skins from blanching process. Due to orchard age and knock-down by wind, it is estimated that each year 20,000 acres of almond orchards may be removed. Based on 90 trees per acre and 200 kg mass per tree, by distributing over the total bearing acreage of 660,000 acres, each 1,000 acre of bearing orchard would generate tree mass of 545 tons annually. By estimation, each 1,000 acres of bearing almond orchard can generate more than 4,800 dry tons of biomass annually at hulling and shelling level including prunings and tree removal. These residues, if processed and used wisely and

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**Received date:** 2010-11-08 **Accepted date:** 2010-12-09

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efficiently, could provide substantial amount of heat and power needed for almond handling and processing (Figure 1). Additionally, advanced conversion technologies may produce liquid and solid fuels and high value materials and chemicals from these residues, bringing extra income to producers and processors. Utilization of these almond residues will certainly enhance the economic viability and sustainability of the almond production and processing industries.

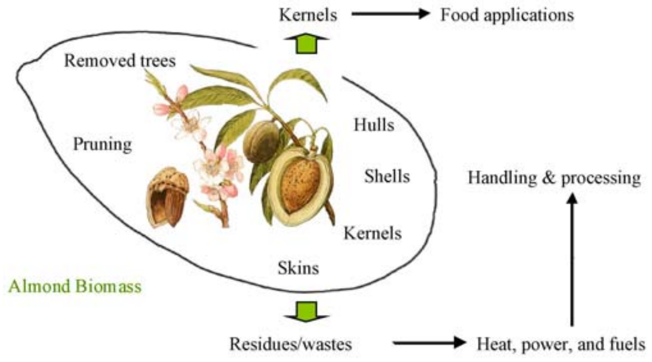


Figure 1 Utilization of almond residues and wastes

This article will provide a review of prior work on the utilization, especially energy uses, of almond residues reported in the scientific and technical literatures, and an assessment of technology options for biomass processing.

## 2 Prior research on utilization of almond residues

### 2.1 Literature search

We searched several major publication databases including CAB, FSTA, Agricola, AGRIS, Academic Search Premier, PubMed, Google Scholar, etc, with search terms such as residues, shells, hulls, pruning, skins, fractionation, antioxidants, phenolics, flavanoids, absorbent/absorption, filtration, gasification, pyrolysis, combustion, co-firing, activated carbons, etc. More than 450 scientific and technical papers and reports covering periods from 1947 to 2010 were found. A breakdown of the key categories is shown in Table 1. The categorization is not meant to be very strict and some overlapping exists among them. As you can see, the majority of work is on extraction and use of antioxidants and making of activated carbons. There is not much on energy uses of almond residues. Hulls and skins are mainly for fractionation, extraction and recovery of valuable compounds while most of shells and pruning are used for making activated carbons, and some for combustion, pyrolysis, and gasification. From the information accessible to us, we are not aware of any large scale commercial conversion operations in the US.

**Table 1 Breakdown of literature search results**

| Category | | Hits |
|---|---|---|
| By residue type | Shells (activated carbons, absorbents/filters, gasification, pyrolysis, combustion, antioxidants, culture media/composite/bedding, carbohydrates) | 106 |
| | Hulls (feed, antioxidants, fiber, gums/polysaccharides, triterpenoids, filter) | 65 |
| | Pruning (combustion, pyrolysis, gasification, activated carbons) | 15 |
| | Skin (antioxidants) | 55 |
| Energy uses | Gasification (shells, pruning) | 7 |
| | Pyrolysis (shells, pruning) | 14 |
| | Combustion/co-firing (shells, pruning) | 6 |
| Non-energy uses | Antioxidants (hulls, skins) | 76 |
| | Activated carbons and biochar (shells, hulls, pruning) | 43 |
| | Absorbents/filters (hulls, shells) | 11 |
| | Others (culture media, feed, carbohydrates, lipids, etc) | 55 |

### 2.2 Energy uses

Table 2 shows the chemical compositions and Higher Heating Values (HHV) of major almond residues. The HHVs are comparable with that of forest residues (18.4 MJ/kg).

**Table 2 Ultimate and proximate analyses and the Higher Heating Value (HHV) of almond residues [1]**

| Residue | Ultimate analysis/% | | | | | Proximate analysis/% | | | | HHV/ MJ • kg$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | H | N | Cl | S | Ashe | Moisture | Volatile Matter | Fixed C | |
| Shell | 50.5 | 6.6 | 0.21 | 0.05 | 0.006 | 0.6 | 3.3 | 80.3 | 15.8 | 18.2 |
| Pruning | 51.3 | 6.5 | 0.77 | 0.05 | 0.035 | 1.2 | 10.6 | 72.2 | 15.9 | 18.2 |
| Hull | 43.0 | 5.7 | 3.28 | 0.01 | 0.008 | 3.6 | 11.3 | 71.2 | 13.9 | 16.2 |

As can be seen from Table 2, different components of the almond residues have different composition, especially the hull as compared with shell and pruning. Therefore, different technologies may need to be employed for their utilization. For example, due to the relatively high nitrogen content in the hull, high temperature gasification may not be appropriate since the $NO_x$ content in flue gas may be too high, and low temperature pyrolysis may be more appropriate for the conversion, and both catalytic deoxygenation and denitrogenation may be required for the pyrolytic bio-oil upgrading.

Almond residues have a energy content in the range of 16-18 MJ/kg[1], comparable with the energy content levels of other lignocellulosic biomass[2]. Shells and hulls are readily available on processing sites. Therefore, almond residues are an excellent alternative source of bioenergy for use on site. Nonetheless, both scientific research and commercial use of almond residues as energy are very limited. Combustion, gasification, and pyrolysis are the focus of prior research. No scientific report on biological conversion (e.g., fermentation) of almond residues has been found in the literature.

Combustion is the easiest way to generate heat and power from almond residues. The heat and power generated may be used in the operations within almond processing plants, and the surplus electricity generated may be sold to local power grids. Direct combustion is the burning of biomass in air to convert biomass into heat, mechanical power, or electricity using various devices, e.g., stoves, furnaces, boilers, steam turbines, and turbo-generators. Direct combustion is simple and employs well-developed, commercially-available technology. Therefore it is not surprising that biomass combustion is responsible for over 90% of the current production of bioenergy. Combustion appears to be a natural choice to get into the energy use of almond residues. However, only a few studies attempted to understand the combustion characteristics of almond residues in different situations and for different purposes[3-10].

Although burning of almond residues sounds really simple, there are a number of factors which could have significant impact on the burning characteristics and efficiency and equipment fouling. The particle size and distribution, density, moisture content, proximate and ultimate analysis, and volatile matters are important physical and chemical properties of combustion fuels. Gonzalez et al[7] combusted three almond residues (shells, pruning, and hulls) with a mural boiler under different conditions. The residues were made into pellets of 5 mm in diameter and 20 mm in length. The researchers found that the pruning and shells burned similar to wood pellets but the hulls did not burn as well. The boiler efficiencies obtained with the maximum fuel mass flow (100%) and minimum draught (0%) were 88.3%, 85%, 78.5% for the pruning, shell, and hulls pellets, respectively, compared with 90.5% for the wood pellets. They also studied mixtures of different almond residues and wood wastes. Mixtures with pruning seem to perform better than others.

Almond shells had lowest N and S, suggesting that the shells are a fuel with lowest $NO_x$ and $SO_x$ emission. Almond residues tend to have high alkaline compounds which cause combustor surface fouling and corrosion. Both almond shells and hulls are considered high fouling fuels[11]. Another study suggested that the low lignin content in almond shells contributed to the relatively low heating value of almond shells compared with olive husk and walnut, hazelnut, and sunflower shells when combusted[4].

No study has been conducted to understand the particle size and density of almond residues on combustion characteristics. In general, burning rate and ignition speed increase with decreasing particle size. But in certain velocity range, larger particles may burn faster than smaller particles[12,13]. The ignition front speed is inversely proportional to the bulk density, while the burning rate tends to decrease linearly with bulk density[12]. Data on the effect of moisture content of almond residues on combustion are not available.

Gasification of almond residues has been attempted by a few researchers[14-20]. Gasification is a process in which lignocellulosic feedstocks are converted to a combustible gas mixture called “synthesis gas (syngas)” or “producer gas” through partial oxidation reactions at high temperatures typically ranging from 700 to 1,100 degree centigrade. Some earlier researchers used the term “pyrolysis” but in fact they meant gasification according to the conditions they used[14,15,20]. Syngas can be burned to produce heat or used in gas engines or gas turbines to generate electricity. Gonzalez et al[1] estimated that a gasifier with a processing capacity of 1,400 kg of almond residue/h will be able to generate 3.99 MW thermal from gasification of almond residues. Gas yield and quality and emission of pollutants are the major concerns of biomass gasification, which may vary with type and moisture content of feedstock, type of gasifier, gasification conditions, etc.

Font et al[14] used a sand fluidized bed to gasify fine particles (0.297–0.500-mm) of almond shells at 745–950℃. The highest gas yield was obtained at 890℃ for ca. 2.3 s. The gas consisted of 1.5% $H_2$, 8.3% $CH_4$, 4% $C_2H_4$, 45% CO, 28% $CO_2$, 0.7% $C_2H_6$, and 0.5% $C_3H_6$ (dry weight basis). The researchers also used a Pyroprobe 100 pyrolyzer to study the effect of particle size, temperature, and catalysts impregnated in the almond shell samples. They found that the particle sizes within the range tested (0.21 to 0.84 mm) and use of catalysts did not have significant effect on gas yields, but the hydrocarbon yields increase with temperature. In another similar study[15], these researchers concluded that the primary decomposition occurs on the bed and the cracking of tars takes place in the hot zone above the bed to the reactor head. The experiments conducted in both studies used very small amounts of samples ranging from a few milligrams to a few grams, representing ideal situation which could be rather different than at larger scales. Tong et al[18] gasified three unpretreated/ unprocessed rice husk, wood wastes, and almond shells using a full scale gasifier. CO, $H_2$, $CH_4$, and unsaturated hydrocarbons $C_nH_m$ are the major product gas components with CO being the highest at around 15%. The syngas from almond shell had the highest high heat value. They found that the CO and $CH_4$ yields from rice husk and almond increased with increasing carbon feed in the range of 200–400 kg/hr but the composition of the hydrocarbon gases were not affected by the carbon feed rate. Almond shells yielded higher $H_2$ than rice husk because almond shells were higher in moisture content (17.2%) than rice husk (12.7%), which may be attributed to the fact that hydrogen is produced from hydrolysis. The product gas consisted of a range of polluting gases (Table 3). Product gas from almond shells had higher $NO_x$ but lower $SO_2$ and tar than the gases from rice husk and wood wastes.

**Table 3 Concentrations of gas pollutants, tar content, and percentage of $CO_2$ and $O_2$[18]**

| | Rice husk | | | | Almond shell | | | | Wood waste | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 700℃ | 750℃ | 800℃ | 850℃ | 600℃ | 700℃ | 800℃ | 900℃ | 650℃ | 700℃ | 750℃ | 850℃ |
| $NO_x$/ppm | 475 | 278 | 139 | 641 | 847 | 1.066 | 1.227 | 595 | 431 | 370 | 151 | 53 |
| $SO_2$/ppm | 555 | 0 | 0 | 280 | 0 | 0 | 0 | 0 | 119 | 80 | 29 | 5 |
| PM10/mg·m$^{-3}$ | 2.8 | 9.4 | 0.5 | 1.3 | 21.5 | 0.9 | 13.0 | 0.7 | 30.9 | 2.4 | 2.1 | 1.0 |
| PM2.5/mg·m$^{-3}$ | 2.4 | 8.5 | 0.4 | 1.2 | 18.4 | 0.8 | 12.8 | 0.7 | 27.8 | 1.7 | 1.7 | 0.9 |
| Tar/mg·L$^{-1}$ | 64.8 | 13.7 | 3.7 | 4.6 | 3.7 | 3.7 | 2.0 | 1.8 | 1.8 | 11.9 | 5.4 | 4.9 |
| $CO_2$/% | 13.4 | 15.7 | 15.3 | 15.3 | 13.7 | 14.3 | 13.5 | 13.6 | 16.8 | 16.1 | 16.1 | 17.0 |
| $O_2$/% | 1.5 | 0.8 | 2.1 | 0.7 | 1.6 | 1.5 | 1.4 | 1.9 | 1.8 | 1.5 | 1.0 | 0.6 |

Rapagna and Latif[16] reported their study on steam gasification of ground almond shells using a fluidized bed gasifier. Use of steam is to enhance gas reforming and further gasification of char (water-gas shift reaction) to increase the yields of $H_2$, CO, and $CH_4$. Their results indicate that gas yields were affected by particle size and temperature. However, for smaller particle sizes, differences in gas yield and distribution practically disappeared in high temperature range, whereas for particles above 1 mm in diameter the yield continued to increase over the entire temperature range (600–800℃), never reaching that attained by the smaller particle systems, indicating the significance of extra- and/or intra-particle thermal resistances for particles larger than 1 mm in diameter. The total gas yields reported in their study ranged from 0.5 to 1.55 $m^3$/kg biomass with hydrogen dominating (around 50% by volume).

Another important processing variable is air flow rate which determines the oxygen input into the system. A higher flow rate (higher oxygen input) produces more gas but less liquid and solid chars (Table 4)[17]. Equivalence ratio, which is the ratio of actual amount of oxygen supplied to the theoretical amount of oxygen required for complete combustion, is another parameter to indicate the oxygen concentration in the feed gas. Tong et al[18] used equivalence ratios in the range of 6%–16% in their study but did not investigate the effects of different equivalence ratio on the gas yield and composition.

**Table 4 Influence of the air flow rate on the fraction yields and HHV of the carbonaceous residues from gasification of almond hulls[17]**

| Air flow rate /$cm^3 \cdot min^{-1}$ | Fractions yields/% | | | HHV char /$MJ \cdot kg^{-1}$ |
|---|---|---|---|---|
| | Char | Liquid | Gas | |
| 50 | 38.2 | 24.0 | 37.8 | 23.8 |
| 100 | 24.2 | 23.0 | 52.8 | 22.2 |
| 200 | 19.0 | 12.1 | 68.9 | 21.1 |
| 400 | 18.0 | 10.4 | 71.6 | 21.1 |

The fractional yields and gas composition vary with type of residue (Tables 5 and 6)[17]. Pruning and shells produce more gas and less solid chars than hulls. The gases produced from pruning and shells had a higher HHV than that from peel, which may be attributed to the difference in $H_2$, CO, and $CH_4$ yields.

**Table 5 Influence of the residue type on the fraction yields and HHV of the carbonaceous residues[17]**

| Residue | Fractions yields/% | | | HHV char /$MJ \cdot kg^{-1}$ |
|---|---|---|---|---|
| | Char | Liquid | Gas | |
| Shell | 11.1 | 13.6 | 75.3 | 25.2 |
| Pruning | 10.0 | 12.1 | 77.9 | 26.2 |
| Peel | 19.0 | 12.1 | 68.9 | 21.1 |

**Table 6 Influence of the residue type on the gas production and HHV[17]**

| Residue | Gas production/$mol \cdot kg^{-1}$ of peel | | | | | | | | | HHV /$MJ \cdot Nm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2$ | $O_2$ | $N_2$ | CO | $CO_2$ | $CH_4$ | $C_2H_2$ | $C_2H_4$ | $C_2H_6$ | |
| Shell | 10.9 | 2.0 | 37.1 | 9.5 | 7.8 | 4.2 | 0.06 | 0.61 | 0.17 | 6.5 |
| Pruning | 9.6 | 1.9 | 37.9 | 11.9 | 7.8 | 3.6 | 0.05 | 0.65 | 0.11 | 6.4 |
| Peel | 7.9 | 2.3 | 35.7 | 9.0 | 7.4 | 2.6 | 0.03 | 0.65 | 0.18 | 5.8 |

There is only one paper related to the modeling of fluidized bed gasification[19]. The author developed a comprehensive simulation program of moving and fluidized-beds (CSFB or CSFMB) to generate temperature, gas, and reaction rate profiles in the bed, or feedboard, or reactor. Almond shells and walnut pruning were tested with air as the gasifying agent and electrical resistance heater to heat the reactor during start-up. The heater is kept under low energy discharge during experiments. Good agreement between the model simulation data and operational data was found.

Syngas clean-up and conditioning has been identified as a key technical barrier to the commercialization of biomass gasification technologies and has the greatest impact on the cost of clean syngas[21,22]. No efforts on clean-up and upgrading of syngas from gasification of almond residues have been reported in the literature.

Pyrolysis is a process to produce liquid fuels or bio-oil from organic materials with combustible gas (similar to syngas from biomass gasification) and char solid (“bio-char”) being the byproducts. During pyrolysis, biomass is degraded to small gaseous molecules at medium high temperature (300–600℃) in the absence of oxygen leaving char solid behind. Pyrolysis of biomass at high temperature is not well understood. Some suggest a five-step process: (1) biomass is heated, (2) volatiles evolve from the organics, and carbonization occurs, (3) outflow of hot volatiles and cooler unpyrolyed fuel volatiles (4) volatiles condense to liquid (tar) with incondensable gas, and (5) autocatalytic secondary reactions (decomposition or repolymerization) take place[23].

The product fraction ratio of bio-oil:char:gas varies primarily with heating rate and biomass composition. The ratios of bio-oil:char:gas for gasification, slow pyrolysis, and fast pyrolysis are 5:10:85, 30:35:35, and 75:12:13, respectively. The bio-oil produced may be refined into liquid fuels or converted to other chemicals. The gas can be used as syngas to generate heat and power. The char can be used as soil amendment agent and fertilizer or made into activated carbons. Biomass pyrolysis has not been broadly commercialized. Complexity and instability of bio-oil are the key barriers to the commercialization of biomass pyrolysis. It is worth noting at this point that pyrolysis is widely used to produce activated carbons from organic materials including almond residues. More discussion on this topic will be provided in the *activated carbon* section.

The first reported study of pyrolysis of almond residues was done by Font at al.[24]. In their study, flash (fast) pyrolysis of almond shells (1–3 grams) was carried out at 400–710℃ with a small experimental fluidize bed reactor with a diameter of 66 mm and the Pyroprobe 100 analyzer. Almond shells were washed, dried, crushed, and sieved to produce three sets of samples with different particle size ranges (0.500–0.297, 0.297–0.210, 0.210–0.105 mm). The effect of particle size on gasification was evaluated using the Pyroprobe 100 analyzer in another study[14], and samples with particle sizes in the range of 0.500–0.297 mm were pyrolyzed using the fluidize bed reactor. The liquid yield reached as high as 65% at 610℃ at high heating rate, which is 20% higher than the liquid yield obtained with slow pyrolysis. At very high temperature, liquid yield was reduced because gasification and cracking was enhanced. In general, a very slow pyrolysis produces very high amount of char solids[25-27], which is desirable for making high energy density chars as fuel or precursors of activated carbons. These results are in good agreement with Gonzalez et al[28] (Table 7).

**Table 7 Fraction yields, proximate analysis, and HHV of the chars and HHV of the bio-oils[28]**

| Variable temp /℃ | Fraction yields/% | | | Proximate analysis/%[a] | | | HHV/MJ · kg$^{-1}$ chars | HHV[b]/MJ · kg$^{-1}$ Bio-oils |
|---|---|---|---|---|---|---|---|---|
| | Char | Liquid | Gas | Field carbon | Volatiles | Ash | | |
| 300 | 47.3 | 41.3 | 11.4 | 60.4 | 38.4 | 1.2 | 26.3 | 13.7(23.6) |
| 400 | 30.6 | 53.1 | 16.3 | 76.9 | 21.2 | 1.8 | 28.2 | 14.1(23.3) |
| 500 | 26.0 | 49.3 | 24.7 | 85.9 | 12.1 | 2.0 | 29.0 | 12.4(24.5) |
| 600 | 23.5 | 44.3 | 32.2 | 91.4 | 5.8 | 2.8 | 29.0 | 12.0(24.6) |
| 700 | 21.7 | 36.3 | 42.0 | 92.4 | 4.7 | 2.9 | 27.4 | 11.6(24.7) |
| 800 | 21.5 | 31.0 | 47.5 | 93.9 | 3.1 | 3.0 | 25.8 | 11.3(24.7) |

| Heating rate /K · min$^{-1}$ | Fraction yields/% | | | Proximate analysis/%[a] | | | HHV/MJ · kg$^{-1}$ chars | HHV[b]/MJ · kg$^{-1}$ Bio-oils |
|---|---|---|---|---|---|---|---|---|
| | Char | Liquid | Gas | Field carbon | Volatiles | Ash | | |
| 5 | 26.3 | 51.5 | 22.3 | 94.3 | 3.7 | 2.0 | 29.0 | 12.4(24.2) |
| 10 | 24.9 | 50.5 | 24.3 | 95.8 | 2.2 | 2.0 | 28.2 | 12.8(24.0) |
| 15 | 22.8 | 50.5 | 26.7 | 95.3 | 2.8 | 1.9 | 28.4 | 13.0(24.1) |
| 20 | 22.1 | 49.9 | 28.0 | 93.7 | 3.7 | 2.6 | 28.4 | 13.7(23.7) |

Note: [a] wt % on dry basis; [b] between brackets are given the water content of bio-oils.

In order to evaluate the potential applications of different fractions from pyrolysis of almond residues, Gonzalez et al characterized physical and chemical properties of bio-oil, char, and gas produced from pyrolysis of almond shells[28]. They found that the char had a high fixed-carbon content (>76%) as well as a high heating value and therefore it could be used as solid fuel. With a large specific surface area, the char is an excellent precursor for making activated carbons. The gas composition was very similar to the syngas from gasification, indicating that pyrolytic gas can be used to heat the pyrolysis reactor or to generate heat/electricity in a gas-turbine/vapor-turbine combined cycle. The bio-oil fraction is composed of mainly aliphatic and aromatic hydrocarbons and hydroxyl and carbonyl compounds, suggesting that the bio-oil is a good source of chemicals of industrial interest, and also can be used as liquid fuel. However, separation and recovery of high value chemicals from the bio-oil will require complex and expensive processes, and the bio-oil is suitable for use as heating oil but its high water content viscosity, corrosiveness, and instability, and poor ignition characteristics make it unsuitable for use as transportation fuels without further upgrading and refining.

Post-pyrolysis upgrading is a common approach to improving and stabilizing bio-oils. Upgrading processes may involve physical or chemical methods. Solvent blending and filtration are physical upgrading methods[29-34], but they are not very effective. Chemical upgrading employs catalytic cracking and reforming such as hydrotreatment and thermal cracking to de-oxygenate the bio-oil. Recent research in this area has made incremental advances in improving the bio-oil quality.

The idea of changing the product chemical profiles using catalysts during pyrolysis instead of post-pyrolysis upgrading has been tested by many researchers. This idea is based on the assumption that some interventions may induce and/or alter certain chemical reactions in Step 2 of the five-step process described above, resulting in different chemical profiles of the volatiles. This is much like an *in situ* upgrading of the biomass pyrolysis vapors, i.e., evolved volatiles from thermal decomposition of organics react directly and immediately on the catalysts pre-mixed with the biomass feedstock[35-38]. Such *in situ* catalytic upgrading of the biomass pyrolysis vapors is also known as catalytic pyrolysis. Catalytic pyrolysis of almond residues was studied by several researchers[24,39-41]. Font and co-workers[24] screened four basic catalysts and six acidic catalysts with which ground almond shells were impregnated prior to pyrolysis. Acidic catalysts especially $FeCl_3$ and $CoCl_2$ produced a significant shifting in the liquid composition. High concentrations of furfural were obtained and acetic acid was reduced. Both basic and acidic catalysts reduced total liquid yields but seemed to favor water production. They further studied the effects of the ratio of catalyst to biomass and the ways catalysts were mixed with biomass[41]. Furfural production and acetic acid reduction were enhanced with increased catalyst amount. Pretreatment of biomass with HCl or NaOH prior to catalyst applications did not make a significant difference. On the other hand, adding catalysts to the almond residues through wet impregnation was much effective than physically mixing the dry solids. It appears that the acidic catalysts promote dehydration reactions, leading to increased formation of 2-furaldehyde and water in the liquid phase[40].

Research on other biomass feedstock also shows that catalytic pyrolysis usually produces additional water and coke-solid residue and thus reduces the yield of the organic phase of the bio-oil. Our study found that chlorides favor production of light oil and especially water solubles and metal-oxides favor heavy oil, and thus total oil yield, while nitrates favor gas production[42]. Bio-oils from current catalytic pyrolysis processes are still not up to the industry standards, primarily due to the still complex chemical composition. However, a positive effect on the quality of the organic phase was noticed, and research has been directed towards the design of selective catalysts for either increasing the production of specific compounds (e.g. phenols) or minimizing the formation of undesirable compounds (e.g. acids, carbonyls). Our more recent study[43] evaluated the effects of metal oxides, salts, and acids including $K_2Cr_2O_7$, $Al_2O_3$, KAc, $H_3BO_3$, $Na_2HPO_4$, $MgCl_2$, $AlCl_3$, $CoCl_2$, and $ZnCl_2$ on microwave assisted pyrolysis of corn stover and aspen wood pellets. The catalyst solids were pre-mixed with the pellets prior to pyrolysis. KAc, $Al_2O_3$, $MgCl_2$, $H_3BO_3$, and $Na_2HPO_4$ were found to increase the bio-oil yield by either suppressing charcoal yield or gas yield or both. These catalysts may function as a microwave absorbent to speed up heating or participate in "*in situ* upgrading" of pyrolytic vapors during the microwave-assisted pyrolysis of biomass. GC-MS analysis of the bio-oils found that chloride salts promoted a few reactions while suppressing most of the other reactions observed for the control samples. At 8 g $MgCl_2$ per 100 biomass level, the GC-MS total ion chromatograms of the bio-oils from the treated corn stover or aspen show only one major furfural peak accounting for about 80% of the area under the spectrum. We conclude that some catalysts improve bio-oil yields, and chloride salts in particular simplify the chemical compositions of the bio-oils and therefore improve the product selectivity of the pyrolysis process.

### 2.3 Non-energy uses

#### 2.3.1 Antioxidants

A paper by Esfahlan et al published on *Food Chemistry* in 2010 provides an excellent overview of non-energy uses of almond residues[44]. The paper has a strong emphasis on antioxidants. The authors tabulated the data from the literatures on the key antioxidants such as vanillic, caffeic, p-coumaric, ferulic acids (after basic hydrolysis), quercetin, kaempferol, isorhamnetin (after acidic hydrolysis), delphinidin and cyanidin (after n-butanol/HCl hydrolysis) as well as procyanidins B2 and B3 in different parts of almond fruits. Table 8 is a summary showing the total phenolics in different parts of almond fruits. Antioxidants in almond residues may be extracted with ethanol, methanol, and warm water[45-49].

The high amount of antioxidants in the skin and hull may be a result of natural evolution for the purpose of protecting the oil-rich almonds from oxidation by penetrating atmospheric oxygen. Almond extracts were found to slow down oxidative processes in food products. Medical studies found that phytochemicals in almonds inhibited DNA niching and human LDL cholesterol oxidation. Antioxidants are regarded as a powerful disease and aging fighting weapon because they protect human cells from attacks by free radicals from food consumptions, smoking, and radiation, thanks to their strong antiviral, anti-inflammatory, anti-allergic, anti-mutagenic, anti-carcinogenic, and anti-cholesterolemic activities. Therefore, extracts from almond residues have a great potential to become natural food preservation additives and dietary/nutriceutical supplements.

**Table 8 Content of total phenolics in different parts of almond[44]**

| Almond fruit parts | Total phenolics content | References |
|---|---|---|
| Kernel | 16.1±0.4[e] | Amarowicz et al. (2005) |
| | 8.1±1.75[a] | Siriwardhana and Shahidi (2002) |
| | 8±1[b] | Wijeratne et al. (2006) |
| | 8±1[b] | Siriwardhana (2006) |
| Skin | 87.8±1.75[a] | Siriwardhana and Shahidi (2002) |
| | 88±2[b] | Wijeratne et al. (2006) |
| | 88±2[b] | Siriwardhana (2006) |
| | 413−342[f] | Monagas et al. (2007) |
| Shell | 2.2[c] | Moure et al. (2007) |
| | 38.0±3.30[d] | Jahanban et al. (2009) |
| Hull | 71.1±1.74[a] | Siriwardhana and Shahidi (2002) |
| | 71±2[b] | Wijeratne et al. (2006) |
| | 71±2[b] | Siriwardhana (2006) |
| | 78.2±3.41[d] | Jahanban et al. (2009) |

Zone: [a] mg catechin equivalents/g ethanolic extract. [b] mg quercetin equivalents/g ethanolic extract. [c] g gallic acid equivalents/100 g shells. [d] mg gallic acid equivalents/g methanolic extract. [e] mg catechin equivalents/g 80% aqueous acetone extract. [f] $\mu$g/g.

While most of the research has been focused on the bioactivity of extracts from almond residues, there are benefits of using processed almond residues directly as additives to food products. First, this would significantly reduce the costs associated with extraction and purification. Second, dietary and soluble fibers in the residues are utilized. However, these benefits do not come without challenges. First, the bioavailability of the bioactive compounds such as phenolics may be low due to the association of many phenolics with cellular structures. Phenolic compounds can range in size from monomers to long-chain polymers such as tannins, and usually exist bound to carbohydrates or as part of repeating subunits of high molecular weight[50-52]. Without certain physical and chemical “liberation” treatments, the phenolics may not have sufficient *in vitro* bioactivities. Second, the crude fibers are so coarse that they will not have the benefits of dietary fibers and may also compromise the sensory attributes of the food products containing these fibers. Finally, the residues many contain flavor spoiling compounds which must be removed before they become acceptable by consumers.

Elis et al[52] reported that lipids and phenolics are encapsulated by cell walls. Mechanical disruption, chewing, and digestion ruptured only the first layer of cells at the fractured surface. In fecal samples collected from subjects consuming the almond diet, they found that the cotyledonary cells remained intact. The intracellular contents would not be released for digestion without breaking the cell walls. Harrison and Were[50] used gamma irradiation to increase phenolic content and antioxidant effect of almond skin. They found that irradiation at 4 kGy (trial I) and 12.7 kGy (trial II) increased the yield of total phenolic content as well as enhanced antioxidant activity of almond skin extracts. Similar results were demonstrated by Teets et al[53]. The increase in phenolic content and antioxidant activity is attributed to the cleavage of covalent bonds, which liberates and activates the low molecular weight phenolic compounds from their glycosylated forms[51].

Prasetyo et al[51] and Teets and co-workers[54,55] tested the antioxidation effects of electron beam irradiated almond skin on meat products. They successfully demonstrated that the antioxidants liberated by the irradiation reduced the oxidation related reactions. These findings suggest that there are opportunities to apply processed almond residues directly to food products without extraction.

### 2.3.2 Activated carbons

The second greatest non-energy use of almond residues is manufacture of activated carbons. World demand for virgin activated carbon is forecasted to expand 5.2 percent per year through 2012 to 1.2 million metric tons. The US is the second largest activated carbon producer in the world. Activated carbons are primarily used for water treatment. Other major applications include separation and purification processes for gaseous or aqueous solution systems and catalytic processes (catalyst and catalyst support). The quality and suitability of activated carbons depend on the specific surface area, pore size, pore structure, volume, ash content[56].

Activated carbons are made mostly from coal and woods. Agricultural byproducts and residues are inexpensive alternatives, and nutshells have been the most used agricultural residues for making activated carbons[56]. Almond shells have been used frequently for activated carbon manufacture[26,57-68]. Almond pruning has also been used to make activated carbons[26,69-71]. The activated carbons produced from fruit shells and stones have high surface areas and highly developed micropore structure compared with the commercial types and those from used tires[56].

Manufacture of activated carbons involves removal of moisture and volatiles from biomass through thermal processes, and activation of the carbonaceous compounds through physical, chemical, and steam treatments[56]. Pyrolysis is the most common process to produce precursors from making activated carbons. Both temperature and heating rate are two most important processing parameters followed by inert gas flow rate and residence time. As discussed earlier, pyrolysis produced more char solids at low temperature and low heating rate. The purpose of activation is to oxidize remaining organics so that the porous structure is further enhanced.

Marcilla et al[65] used a two-stage thermal process to produce activated carbons from almond shells. In the first stage, almond shells were heated at 275 to 400℃ at the low heating (3–4℃/min) followed by a second stage at the high rate (ca. 3,000℃/min) up to 850℃. The products treated this way exhibited a better porous structure than those obtained treated with a single heating up to 850℃ at both heating rates. The second heating step in the two-stage process may act as an activation treatment. Other activation methods such as air activation, steam activation, $CO_2$ activation, and acid activation have been tested on almond residue derived carbons[60,61,70,72]. $CO_2$ is the most common chemical activation method, partly because it is clean and low cost. Toles et al[60] studied both the $CO_2$ and steam activation processes combined with an air oxidation step in the production of granular activated carbons (GAC) from almond shells. They looked at the surface area, attrition, surface charge, copper ion ($Cu^{+2}$) uptake, adsorption of a mixture of six polar and non-polar organic compounds and estimated cost of carbon production as a function of different treatment combinations (pyrolysis temperature and time, activation temperature and time, activation method, oxidization). They concluded that the steam-activated, unoxidized and oxidized carbons appear to be the most economical GACs to manufacture and also the most economical for removal of copper ions and organic compounds. They presented cost analysis assumptions (Table 9) and results (Table 10) in their paper, which may be of interest to the readers of the present review and are therefore included here for reference. The largest difference between the two activation methods is in the electricity usage according to Table 9.

### 2.3.3 Other non-energy uses

Almond residues have been used directly or after some treatments as absorbents for removal of metals and dyes[73-78], feed[79-92], culture media[93-104], and raw materials for extraction of xylo-oligosaccharides[105-109], polysaccharides[105,110,111], and dietary fibers[90,112]. These uses are beyond the scope of this review. Interested readers are encouraged to read the review papers by Esfahlan et al[44] and other references provided.

**Table 9 Assumptions made for scaled-up, production cost comparisons[60]**

| Inputs and consumptions | Steam activation | $CO^2$ activation |
|---|---|---|
| Shell input/kg・$d^{-1}$ | 13.636 | 13.636 |
| $CO_2$ usage/kg・$d^{-1}$ | — | 13.636 |
| Water usage/$ft^3$・$d^{-1}$ | 25 | — |
| Natural gas usage/$ft^3 \times 10^6$・$d^{-1}$ | 61.8 | 78.8 |
| Electricity usage/KWH・$d^{-1}$ | 4,075 | 7,501 |
| Carbon yield/% | 16 | 16 |
| Operating days/year | 320 | 320 |
| Active operating hours/d | 24 | 24 |
| Daily carbon output/kg・$d^{-1}$ | 2,180 | 2,180 |

**Table 10 Production and adsorption cost estimates for steam-activated and carbon dioxide-activated almond shell GACs[60]**

| Treatment[b] | Production /S · $\mathrm{kg}^{-1}$ | $\mathrm{Cu}^{2+}$ adsorption /S · $\mathrm{mol}^{-1}$ $\mathrm{Cu}^{2+}$ | Organics adsorption / S · $\mathrm{mol}^{-1}$ |
|---|---|---|---|
| Steam activation | | | |
| 1-7-2-8 (7.0 mL/min) | 1.54 | 4.16 | 2.96 |
| 1-7-2-8 (7.0 mL/min-ox.) | 1.91 | 3.67 | 3.60 |
| 1-8-2-8 (7.0 mL/min) | 1.54 | 4.40 | 2.40 |
| 1-8-2-8 (7.0 mL/min-ox.) | 1.91 | 4.78 | 3.14 |
| $\mathrm{CO_2}$ activation | | | |
| 1-7-2-8 (75% $\mathrm{CO_2}$) | 2.56 | 6.74 | 4.63 |
| 1-7-2-8 (7% $\mathrm{CO_2}$-ox.) | 2.93 | 5.05 | 5.59 |

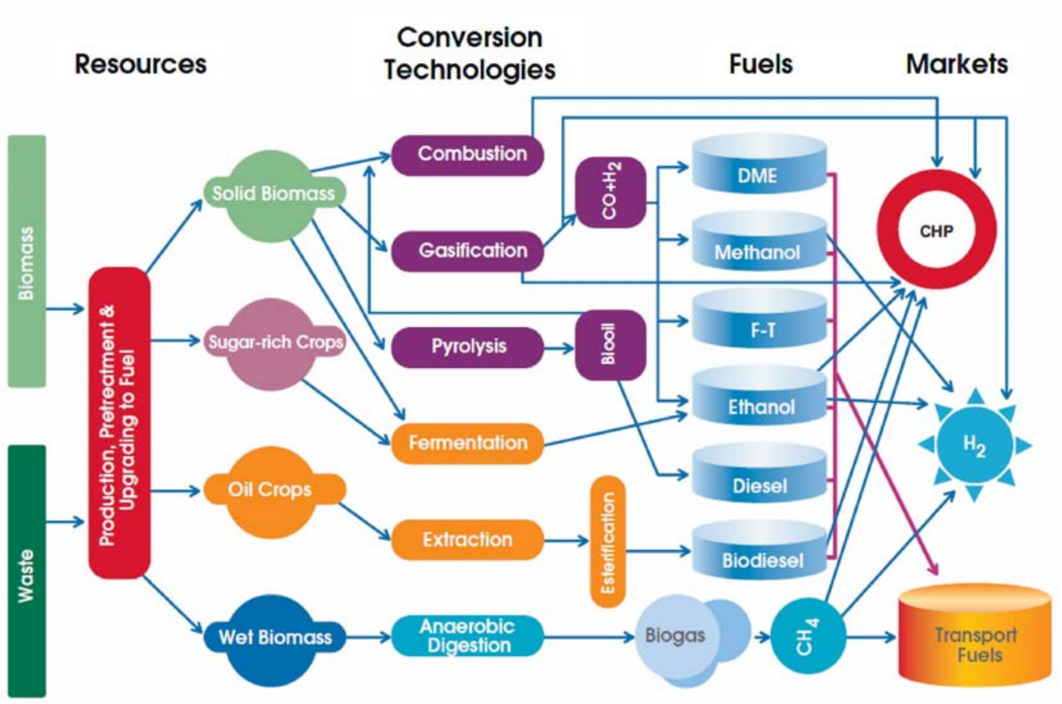
Note: [a] Adsorption cost estimates were determined from the production cost values (S/kg) and the amounts of $\mathrm{Cu}^{2+}$ or total organics adsorbed (mol/kg). [b] Treatment conditions consist of number sequences 1-7-2-8, etc. which refer to pyrolysis times (1 h) and temperatures (700℃) and activation times (2 h) and temperatures (800℃).

## 3 Technology options

### 3.1 Individual technologies

In addition to what have been discussed above, a wide range of other technologies may be used to convert almond residues to different forms of energy, chemicals, and materials (Figure 2). However, the unique physical and chemical properties of almond residues make fermentation and anaerobic digestion unfit options. Use of almond residues with or without treatments appears to be the easiest option but it may not capture the best values of these residues. Therefore, extraction and thermochemical conversions have the best potential to bring extra income to almond producers and processors.

While combustion is an easy and feasible option, most of the large almond processors could use only a fraction of the residues to supply the heat for their on-site operations. Therefore combustion has limited potential for almond processing facilities. Gasification faces a similar situation. The gas produced must be used locally because storage and transportation of the gas to elsewhere are economically and technically impractical. Unless low cost syngas reforming processes can be devised, gasification will limit its use to small scale almond producers and processors. Pyrolysis is technically less mature than combustion and gasification. However, it has a great potential in converting solid almond residues to transportable liquid fuels and activated carbons. The syngas produced from the pyrolysis process may be used to power the pyrolysis itself and other operations on site. R & D efforts are needed to develop cost effective equipment and improve the quality and stability of pyrolytic liquid through manipulating the pyrolysis conditions and post-pyrolysis upgrading.



Note: DME: Dimethyl Ether; F-T: Fischer-Tropsch; CHP: Combined Heat and Power

Figure 2 Bioenergy from biomass through different pathways[113]

Pyrolysis is a potentially key player in the bioenergy industry. The US DOE and USDA have a strong interest in producing liquid transportation fuels from biomass in order to replace fossil based fuels. Several research funding solicitations have been issued by DOE/USDA specifically to target liquid fuel production from cellulosic biomass. Very recently, there is a surge in interest in biomass pyrolysis because the biochar, which is usually a byproduct of biomass pyrolysis, if applied to soil, is considered one of the best options for carbon sequestration, soil improvement, and pollutant absorption. Therefore, we believe that pyrolysis should be considered favorably for almond residue conversion.

### 3.2 Commercial technologies

Commercial/near commercial pyrolysis facilities are very limited with just four North American companies using pyrolysis to produce bio-oil and other products[114]. They are Ensyn Technologies, Inc. (Canadian), DynaMotive Energy Systems Corp. (Canadian), Advanced Biorefinery (Canadian) and Renewable Oil International (US). Ensyn and DynaMotive have plants up and running while Renewable Oil International is a small startup company with experience in demo systems. Another Canadian company Agri-THERM Inc. is testing its demo system. Current commercial plant sizes are in the range of 45 to 100 tons per day. Current Ensyn commercial scale plants produce mainly barbecue flavors and colorants. A big challenge for the Ensyn and DynaMotive systems is the cleanup of the bio-oils and pyrolytic gas because of the large presence of ash particles, which can be attributed to the fact that these systems require fluidizing fine ground feedstocks. Table shows a list of world wide pyrolysis plants with reactor type and capacity.

**Table 11 Worldwide current biomass pyrolysis operating plants[29]**

| Reactor design | Capacity (dry biomass feed) | Organization or company |
|---|---|---|
| Fluidized bed | 400 kg/hr (11 tons/day) | DynaMotive, Canada |
| | 250 kg/hr (6.6 tons/day) | Wellman, UK |
| | 20 kg/hr (0.5 tons/day) | RTI, Canade |
| Circulating fluidized bed | 1,500 kg/hr (40 tons/day) | Red Arrow, WI; Ensyn design |
| | 1,700 kg/hr (45 tons/day) | Red Arrow, WI; Ensyn design |
| | 20 kg/hr (0.5 tons/day) | VTT, Finland; Ensys design |
| Rotating cone | 200 kg/hr (5.3 tons/day) | BTG, Netherlands |
| Vacuum | 3,500 kg/hr (93 tons/day) | Pyrovac, Canada |
| Other types | 350 kg/hr (9.3 tons/day) | Fortum, Finland |

These commercial biomass conversion units are large scale systems requiring large capital investment. Most small scale units are in pilot testing stage and are based on fluidized bed gasification technology where capital costs are still relatively high. Small scale microwave assisted pyrolysis/gasification system has the advantage of less biomass grinding or particle size requirement and higher syngas energy values.

In California, USA, almond growers produces more than 4,800 dry tons of biomass byproducts per 1,000 acres bearing almond orchards each year. Based on a 1,000 acres of almond farming operation with hulling and shelling facility, installing a small scale bioenergy conversion system based on using pyrolysis and/or gasification technology can bring in more than $120,000 annual income. One of the major costs in bioenergy utilization of biomass is the cost for transportation of biomass. Considering characteristics of almond farming and processing, it would be feasible to install a small scale unit in a hulling/shelling or almond processing plant, and the unit should be able to generate streams of biofuels that may be economically transferred to off-site for upgrading in addition to heat and electricity that can be consumed on site.

## 4 Conclusions and recommendations

Almond residues are excellent feedstocks for production of energy and value added products. Almond residues store a large amount of energy which can be converted to several forms of usable energy through a number of commercially available processes as discussed in the review. However, from the information accessible to us, we are not aware of any large scale commercial conversion operations in the US. Pyrolysis is believed to be the reasonable choice to convert almond residues to liquid fuels, biochar, and activated carbons. Current commercial pyrolysis technologies, like most gasification processes require energy intensive grinding operation and face problems with high ash contents in the bio-oil. Highly scalable technologies are desirable because of the distributed nature of almond production.

Almond residues especially skin and hulls are high in phytochemicals such as antioxidants. Extraction of phytochemicals from the residues before the residues are converted to energy presents an excellent business opportunity. New processes to turn almond residues especially almond skin and hulls to food additives rich in dietary fibers and antioxidants with improved sensory attributes are highly desirable.

Therefore, we recommend the biorefinery approach to the utilization of almond residues. Biorefining is a concept derived from petroleum refining. A biorefinery uses biomass as feedstock as opposed to fossil resources used in a petroleum biorefinery. The goal of biorefining is to produce a wide range of products such as fuels, materials, chemicals, etc., from biological resources, much like what we make from fossil resources. Because biomass is not a uniform feedstock, several biorefinery platforms such as biological platforms and thermochemical platforms have been proposed based on the unique characteristics of the biomass feedstocks used. A biorefinery uses a portfolio of conversion and refining technologies and may be integrated with biomass feedstock production. An integrated biorefinery is capable of producing multiple product streams and thus multiple income streams from a single biomass feedstock and, therefore, more economically viable than single product-based production schemes (Figure 3).

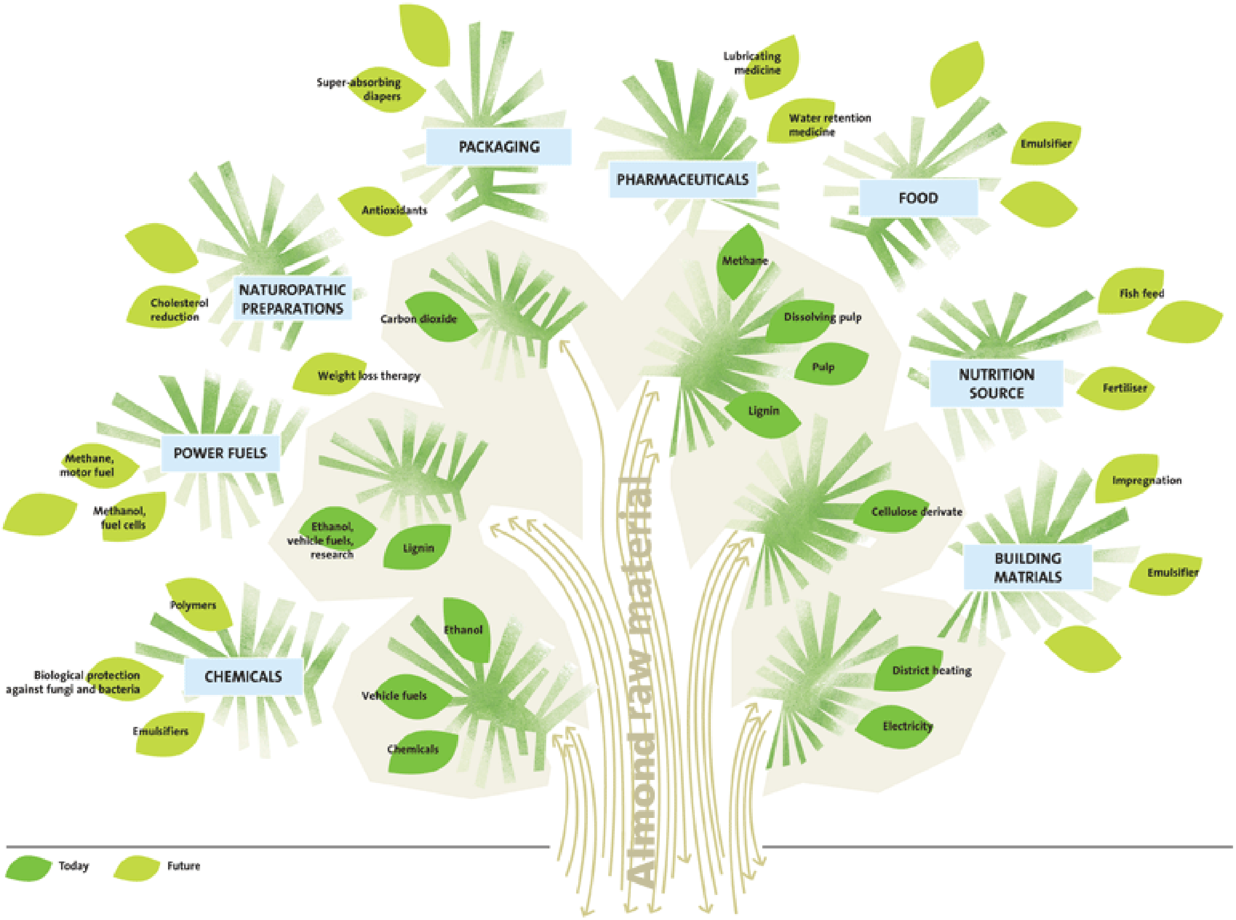


Figure 3 Product possibilities from a biorefinery

It appears that there are multiple routes to the utilization of almond residues with different product targets, especially for almond hulls that have relatively high level of nitrogen in composition that consequently generate more contaminants during bioenergy conversion. A systematic approach, oftentimes, a sequential processing scheme, may maximize the utilization efficiency at lowest overall costs. For example, almond hulls may be first extracted for high value compounds such as antioxidants, protein, and sugars, and the remaining residues may then be converted to energy and fuels. The energy generated may be used to power the processing operations.

## Acknowledgments

We appreciate the financial support provided by the Almond Board of California for most of this work, and Karen Lapsley, Gabriele Ludwig, Robert Curtis, and Tim Birmingham of Almond Board of California for their valuable reviews and comments.

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