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Long-Term Strategies for Supplying Nitrogen to Crops

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LONG-TERM STRATEGIES FOR SUPPLYING NITROGEN TO CROPS

by

Vincent P. Gutschick

ABSTRACT

Raising food for present population requires nitrogenous fertilizers in addition to indirect management of the biosphere's nitrogen cycle. The Haber process for making the ammonia base of fertilizers is increasingly pressed by shortages of energy, while only minor improvements are still possible. I discuss the Haber process and 15 alternatives for increasing the nitrogen available to crops using less fossil energy. These alternatives span technology of fertilizer synthesis, farm management and technology, crop genetics, and market management. They were selected by criteria of energy-efficiency and of meeting the numerous biological/physical constraints posed by soils and plants. The alternatives vary in scope and efficacy due to scientific, economic, and political constraints which need be appreciated by policy-makers and researchers alike. I conclude that the Haber process will be the mainstay for nitrogen-nutrition of crops for 50 years, and a few alternative strategies — especially in farm management, but little in crop genetics — will slowly achieve a partial replacement of the Haber process. Full replacement in the longer run requires commitment within a few decades to developing the strongest alternatives.

I. THE PROBLEM OF FERTILIZING THE WORLD'S CROPS

Farmers may justly be said to work harder for nitrogen than for any other nutrient of their crops, with the partial exception of water, The advanced state of agriculture today is based on many past gains - in breeding of crops, disease control, irrigation, but nitrogenous fertilizers are a *sine qua non*. These fertilizers are necessary to support today's burgeoning world population on limited land. They increase the average yield of crops per unit area to levels near five times[1] those attainable with natural supplies of soil nitrogen. Natural supplies are so low as to limit the growth of plants in most regions.[2] The "Green Revolution"[3] which sustains the hopes of less-developed countries rides on nitrogenous fertilizers. Manufacture and use of such fertilizers — 40 million metric tons[4,5] annually — are massive enterprises in today's agriculture and world trade.[4,5] Fertilizer-manufacturing plants alone are a capital investment totalling billions of dollars U.S.

Although virtually all forms of "fixed nitrogen" are equivalent in their value to crops,[2a,6] about 70% of the total by weight[7] derives from one origin, ammonia produced by the Haber process and its modifications.[8,9] While the Haber process, and the "reforming" of hydrocarbons to generate hydrogen for it, are together very efficient in energy and in costs, it still requires the energy in more than 1000 cubic meters[10] of natural gas to produce every metric ton of ammonia. The 8 million metric tons[4,5] of fixed nitrogen produced in the U.S. alone consume [11,12] annually about 1.6% of natural gas and 0.5% of total energy in this nation. Because natural gas and any equivalent energy are increasingly scarce, while demand for fertilizer must rise, there is grave concern about (1) our best source, the Haber process, pricing itself beyond viability; (2) possible alternatives to ammonia or other fertilizer; and (3) world food supply. Will there be general famines in the next 50 years as fossil fuels are exhausted to low levels? Even if use of more labor and more land keeps up total food production, the cost will be high in lost wild land (and its gene pool for occasional use by crop breeders). Because energy and fertilizer are both traded heavily in world markets in an unbalanced fashion, will political disruptions occur in all nations even if supplies of both are acceptable in size? Fortunately, there are ways to use fixed nitrogen more efficiently and to increase "free" biological contributions; there are ways to make our last available fuels work efficiently for making ammonia -- including nuclear energy by a technical *tour de force* -- and one may predict with some confidence that peaceful readjustments in use of energy will favor the uninterrupted manufacture and use of fertilizer, or use of alternative biological routes. This good fortune, to come to fruition, demands great efforts in economics, engineering, and science with full knowledge of all the "strategies" for the complete development of our resources of fixed nitrogen. It is these strategies and their limits/hopes which I have aimed to present here...to be acted upon by policy-makers, scientists and engineers.

II. POSSIBLE STRATEGIES FOR MAINTAINING OUR RESOURCES OF NITROGEN FOR NOURISHING CROPS

A. Premises: Scientific and Economic

I accept the premise that to supply enough food, high levels of fixed nitrogen must continue to be supplied to crops. Contributions to the effort will be made by synthetic fertilizers; and by much-improved agricultural management which favors enhanced biological fixation of nitrogen, as well as better use of all nitrogen. In general I ignore other sweeping measures for matching food to population, measures that are equally necessary such as stabilizing world population. I also leave to others the partly related measure of increasing available energy, which would enable the Haber process to be used indefinitely. At present, however, energy resources are shrinking. A great many workers are attempting these other measures, in efforts described very often in popular, technical, and academic accounts. I have concentrated here on a measure which is equally deserving but less organized: supplying increasing amounts of fixed nitrogen to crops efficiently, using decreasing amounts of fossil energy.

The present best source of fixed nitrogen to push yields higher is ammonia from the Haber process plus hydrocarbon-reforming (reforming/Haber, or r/H). The manufacture is highly perfected, even if begining to be plagued by a scarcity of energy. Therefore I discuss the future of r/H in detail, and also expound upon 15 other strategies of providing abundant nitrogen to crops. These strategies (one alone, or in some combination among themselves) ultimately may support our agricultural needs (1) with less fossil energy, (2) where needed most, and (3) at bearable costs. They are based on several premises:

(A) For manufacture of synthetic nitrogen, various energy sources can be traded, such as nuclear for natural gas (with some added technology).

Energy-efficiency of the *complete* manufacturing process is crucial, so one must use various sources in their best ways. E.g., nuclear energy is to be used for its heat directly, without intermediate conversion to electricity which is easy and perfected but wasteful (App. C, Sec. II.B).

We need to conserve fossil energy in general. A way to conserve which is directly relevant to supplying crops with nitrogen is to decrease the use of energy in tilling fields while keeping soil in good tilth by other means.[13-15]

There are limited supplies of nonfossil, renewable energy, including residues from crops themselves.[16-20] Their use for energy is justified only if the loss of their nitrogenous value is more than compensated by generating equivalent energy from them.

If a shortage of energy develops, energy for manufacture of fertilizer is last to be curtailed, compared to other, replaceable uses in agriculture or in general.

(B) Biological sources of fixed nitrogen include both crops themselves (legumes) and free-living microbes. One must recognize the *limited* ecological niches for present "fixers," due to nutritional requirements and limited distribution of species (App. C, Sec. V).

The development of new species of fixers by breeding or genetic engineering has been discussed.[11] One must recognize the biological limits inherent in the present microbes or genes which we hope to adapt in these fashions.

Biological fixation consumes some of its energy derived from the sun or from soil humus. It is possible to optimize the availability of energy in the plant, such as by suppressing photorespiration (App. C, Sec. V.E).

Crop wastes left in fields or ending up as urban waste have nitrogenous value that can be reclaimed more completely than is done now.

(C) The predominant direct source of nitrogen for crops as a whole is inorganic nitrogen in soil, from whatever ultimate sources.

There are biological and physical competitors to uptake from soil by the plant (App. A). These can be suppressed by chemicals and by good agricultural management, using knowledge of the nitrogen cycle among air, soil and water.

Uptake of ammonia is somewhat less costly to yield than uptake of nitrate, the other major form in soil. (App. B).

(D) After assimilation from the soil, nitrogen is used by species of crops with widely-varying efficiencies to make edible protein.[14]

We can choose to plant more area to the crops with highest nitrogen-efficiencies.

We should also consider new foods, such as algae which can be self-sufficient in nitrogen[21] or else protein from inedible leaves.[22]

Other strategies will succeed in reducing the Haber process only over a very long time, exceeding 50 years. In this crucial period of development, the r/H process will remain necessary even at very high costs. Decisive action will be necessary on the part of economic and scientific policymakers and of scientists and engineers themselves, to ensure that a sufficient mix of alternatives is ready. This report has a final goal of clarifying the needed action.

B. Types of Strategies

Broadly there are five approaches to nourish crops with nitrogen, four of which use notably less fossil energy than the first. (1) Make ammonia for fertilizer conventionally by the reforming/Haber process, perhaps with slightly improved efficiency. (2) Make ammonia or nitrates by more radical technologies which partly or wholly replace the r/H process. (3) Induce a greater fraction of soil nitrogen to be taken up by plants, instead of being lost to competing processes in soil or to cropping without return of wastes; this can be done with better agricultural management. (4) Develop new biological sources of fixed nitrogen — root symbionts, leaf symbionts, new varieties of major crops genetically capable of fixation, new varieties of legumes with more active fixation, algal crops capable of their own fixation. (5) Convince people to use the more-efficient crops in preference to less- efficient ones, and find ways to use a greater portion of existing plants (their leaf protein).

It is desirable to discuss all 16 detailed strategies together in this report, rather than piecemeal as represented in past literature. All strategies are certainly not appreciated and understood equally by makers of public policy or researchers seeking to apply their talents. Neither are the various strategies ranked, funded and pursued in order of their merits by persons who are individually well-informed about only a few of them. For example, I have researched scientific and economic constraints on transferring nitrogen-fixing genes into major crops. I am led to conclude that this work should not be funded as a large program. Its success lies far in the future, and most of the (costly) background work in genetic engineering applies to other, more pressing areas such as medicine. Public funding and most of the research should be in these other problem areas, with nitrogen-fixing research as a peripheral interest or "spin-off."

Aiding such decisions on development and research is the goal of this report. I also hope to suggest interesting new areas of development and research to people.

C. A Guide to The Report

Appendix C contains the heart of this report, a full discussion of each strategy. It is an appendix simply because it is long and for some persons and purposes is too detailed. Appendices A and B present a critical background on concepts about plants and soil which may or may not be necessary for individual readers. They precede "C" logically but not in importance.

Each strategy has a (possibly) fascinating history or else currency of interest...ranging from the historical detective story of learning how a few plants fix nitrogen, to the current great promises and great dangers of genetically engineering more plants to do so. I have skipped almost all history for brevity. I recount for each strategy the scientific basis - and economic basis when it is not totally speculative. Each strategy has degrees of hope and hazard set by its scientific, economic, and political limits, which are all known only between rather broad bounds. I have tried to clarify these bounds firmly, and have subjectively estimated how successfully each strategy will be applied in the coming decades.

III. MY CONCLUSIONS CONCERNING THE RATE OF SUCCESS FOR ALL STRATEGIES

Detailed conclusions and upper/lower limits are noted in paragraphs denoted as "prospects" in App. C.

Manufacture of fertilizers via the reforming/Haber process for ammonia from natural gas will be our mainstay for 50 years. In as severe an energy shortage as can be envisioned for this time, it will be kept running preferentially at any needed level. Political conflicts over allocation will arise, however. The fertilizer will be used more efficiently by suppression of losses after application. Application at a lower rate still certain to give good yields will be practical but not universal; it depends upon development of accurate field tests for nitrogen-sufficiency, and also upon the uncertain prospect of less-intense economic competition in the artificially structured agricultural markets. Conservation of energy so that the fraction used for synthesis of fertilizers has a bearable cost will not be practiced in the world ergonomy in timely fashion. Agriculture will be pressed to use expensive fertilizer, to cut use of fossil fuels in tilling in favor of more labor on-farm, and to use some crop residues as the renewable fuel methane. New processes for making nitrogenous fertilizers, such as oxidizing nitrogen thermally, will never succeed. Sources of hydrogen for the Haber process to replace reforming of natural gas will expand to include nuclear fuel and coal. While nuclear fuel and coal are still fossil/nonrenewable, their use gives a greater flexibility to manufacture of ammonia. (Coal gasification to *hydrogen* for captive use at a Haber plant will use simpler, surer technology than gasification to methane for general use; the former will be perfected more quickly and with less environmental distress than the latter. Thus a long-term supply of energy for the Haber process at bearable costs is virtually assured. Nuclear thermochemical generation of hydrogen is likely to be a lesser contributor than coal.) Purely biological sources for increasing fixation of nitrogen will fail to be developed and to contribute significantly, except for one: legumes will become nearly self-sufficient in nitrogen because chemical suppression of yield-sapping photorespiration will become practical. Reclamation of nitrogen-rich urban wastes - which wastes are the fate of the bulk of nitrogenous value in harvested crops - will not be practiced on a significant scale. The use of crops that are more efficient in converting a given amount of nitrogen into edible protein will get only marginal attention, because of political problems in reassigning artificial economic subsidies to crops worldwide. Radically new "crops" such as protein from leaves will gain moderate acceptance and give moderate relief to food shortages.

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APPENDIX A

THE NITROGEN CYCLE AMONG PLANTS, SOIL, WATER, AND AIR - AND ITS AGRICULTURAL MANAGEMENT

I. FORMS OF NITROGEN AND PROCESSES OF INTERCONVERSION

Common green plants are *auto*trophic organisms, able to grow on the inorganic nutrients in the environment. As a whole, plants are so successful as to grow to the limits of local nutrient supplies. The limiting nutrient in most *natural* habitats is nitrogen,[2] because the vast bulk of nitrogen in air or soil is unassimilable by and unavailable to plants. (In some habitats other nutrients are limiting, such as water —— especially episodically; carbon dioxide; or chemical elements needed in lesser proportion such as phosphorus or metals.) Empirical evidence that nitrogen is limiting includes the almost-universal large increase in biomass of plants in an ecosystem in response to nitrogenous fertilization - called eutrophication when inadvertent. Nitrogen is needed in quantity because non-woody plants average 2% N by weight in their dry matter; new growth may amount to tens of thousands of kg/ha/yr in dry matter.

Only a few chemical forms of nitrogen are available to plants, principally nitrate and ammonium ions in soil. Elemental nitrogen in air is not available, although it functions as the largest reserve (more than rock or humus) for plants with the help of soil microbes or "minor" chemical reactions in the atmosphere. Soil humus is likewise a reserve, formed by death and mobilized for growing plants via decay. Chemical and biochemical transformations among the various forms of nitrogen result in dynamically varying amounts of assimilable nitrogen as I now discuss.

Nitrogen is chemically a very versatile element[24,25] able to exist in oxidation states from +5 to -3 as Fig. A-1 shows. Five major natural forms are indicated: fully-oxidized (+5 state) nitrate ion, NO_3^- ; partially-oxidized (+3 state) nitrite ion, NO_2^- ; elemental (0 state) nitrogen, N_2 ; partially reduced (+2 state) amide groups, $-NH_2$, in organic amino acids, as bound into the proteinaceous part of humus; and fully reduced (+3 state) ammonia, NH_3, or its cationic, protonated equivalent of ammonium, NH_4^+ . Oxidation states intermediate to these, and other representatives of the above states, occur free in the biosphere only to negligible extents. More commonly

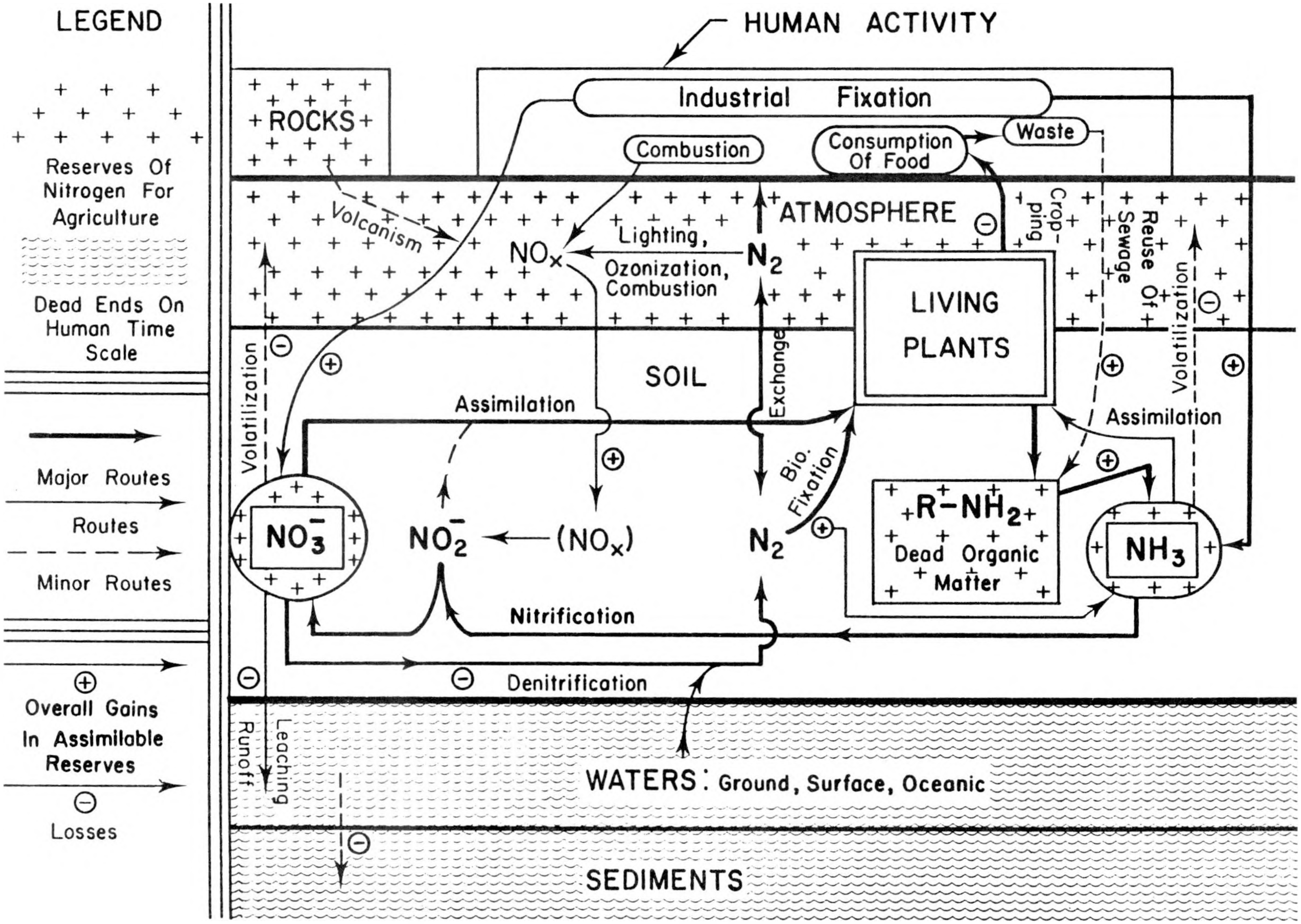

Figure A-1. Agriculturally important forms of nitrogen and the processes by which they are related.

their alternatives are bound, biosynthetic intermediates, such as diimide HN = NH which occurs in minute concentrations bound to nitrogen—fixing enzymes. Of these five major forms, nitrate and ammonia are assimilated readily,[6] nitrite less readily. Others are unavailable or even toxic. Small amounts of free amino acids[26,27a] occur in soil , but except for alanine, aspartic acid, and glutamic acid, are not assimilated. Soil humus is thus assimilated only after it decays to ammonia. Amino acids formed at roots of selected species by symbiotic "nitrogen-fixing" bacteria, in contrast, are readily transported across the intimate bacterial-plant contact. Internally, plants or their symbionts route all their assimilated inorganic nitrogen—be it NH_3 , NO_3^- , or N_2 — through the ammoniacal stage NH_3 in order to incorporate it into amino acids, chlorophyll, nucleic acids, etc.

Chemical and biochemical conversions among forms of nitrogen may be grouped into five categories: (1) sources of assimilable nitrogen, converted from unassimilable forms; (2) sinks or losses; (3) neutral transformations interconverting two assimilable forms; (4) transports of assimilable forms, usually out of the soil and into bodies of water, thus being losses from the viewpoint of agriculture; and (5) assimilation of inorganic nitrogen into plants — the ultimate use from the viewpoint here.

A. Sources

(1) Complete decay or ammonification is the microbial conversion of dead plant and animal material to inorganic material such as carbon dioxide, water and ammonia. It is absolutely necessary for the fluorishing of higher plants, as otherwise virtually all nitrogen would be tied up in dead material (purely chemical decay is geologically slow). Decay is due to a wide variety of bacteria, yeasts and other microbes, and this flexibility allows it to proceed efficiently under many conditions. Temperature, hydration, soil aeration and other gross environmental factors affect the net rate and the mixture of end products. Aerobic, contrasted to anaerobic, decay leads to more-assimilable products such as sulfate and ammonia versus gaseous hydrogen sulfide or nitrogen. Fortunately, decay needs little help from human management and is virtually impossible to suppress in the field by accident or design. On a global basis, decay is the principal source of assimilable nitrogen. New fixation makes up a small but crucial annual deficit.

(2) Biological fixation of atmospheric nitrogen to ammonia or amino acids is achieved only by some genuses of the primitive or procaryotic microbes, either bacteria or blue-green algae.[21,28,29] It mobilizes the vast reserve of atmospheric nitrogen. There are natural abiological fixations also, but on a lesser scale than biological fixation --- perhaps 45 Tg (million metric tons) annually[30] from the former compared to 175 Tg (136 Tg on land) from the latter. Two modes of biological fixation occur: free-living and symbiotic. Free-living blue-green algae and bacteria populate virtually the whole range of soils and some plant surfaces. They excrete excess ammonia while alive[21e] and contribute organic nitrogen upon death and decay. Their metabolically-wasteful excretion may be due to their extreme simplicity. Free-living algae are usually photosynthetic and aerobic. Thus they are only weakly competitive with higher plants for energy and positively helpful regarding nitrogen. Free-living bacteria are usually aerobic and heterotrophic, growing on decayed matter if it is not rich in nitrogen.[31a] Much less widely distributed are the symbionts, mostly bacteria of the genus *Rhizobium* found within roots of legumes. They utilize the carbohydrate (cH) supply of the host plant and in return export amino acids. Any fixation is energetically "uphill" from N_2 + H_2O by *ca* +340 kJ per mole of NH_3 formed. This energy is supplied by respiration, using an external supply of cH (symbionts and heterotrophic free-livers) or an internal supply (photosynthetic free-livers). Efficiency of using the cH energy varies from 13% in symbionts (see App. B, Sec. II.B) to one-tenth[32] this, or about 1%, in the average free-living microbe. Thirteen percent is only slightly below par for biological processes, and remarkable for accomplishing a difficult reaction under mild conditions. Free-livers tap energy — as in humus — which is not available to the green plants so that even inefficient fixation shared with green plants benefits the plants. Symbionts cost the green plant perhaps 6% of its yield (App. B, Sec. II.A) but do guarantee a local supply of fixed nitrogen.

On a local basis, the amount of biologically-fixed nitrogen available annually depends broadly upon soil and vegetation types and temperature. Tropical soils surpass temperate soils in fixation per unit area; grasslands and marshes exceed forests; agricultural land as a whole achieves the average for all land despite extreme variations in types of agriculture. Hardy and Holsten[24] estimate annual rates of 55-146 kg of nitrogen fixed per hectare for leguminous crops, 5 for nonlegumes as crops, 30 for rice fields, 25-30 for other soils and vegetations. Agricultural land requires annually from 30 to more than 100 kg/ha (under intensive cropping) of new fixation, biological or artificial. On intensively cultivated land in developed countries, cropping drains on nitrogen exceed the capacity of decay plus biological fixation. Nitrogenous fertilizers are used, but their contribution is slightly less than additive to biological fixation because they suppresses the latter. (When fixed nitrogen is superabundant, microbes are not stimulated to fix their own.[33])

(3) Atmospheric chemical reactions are abiological but still natural (or at least inadvertent industrial) sources of fixed nitrogen: lightning, combustion and sunlight-driven ozonization. Direct ionization of air by lightning (occurring in the troposphere) and in ozonization (in the upper atmosphere) induces combination of N_2 and O_2 to give nitrogen oxides. High temperatures in combustion do the same. Combustion may be natural, such as forest or grassland fires due largely to natural causes, or due to human activity such as use of internal combustion engines. These two contributions may be about equal now. The nitrogen oxides are washed out of the atmosphere and into the soil by rains and are oxidized microbially to assimilable nitrite and nitrate. Total contributions from each source are estimated[30] as 10, 20, and 15 Tg per year for lightning, combustion and ozonization, respectively, distributed over the whole earth. Given that perhaps half of these products fall over land (*vs* sea)[34] and that 10% of land is cultivated, the above processes contribute only *ca* 2.2 Tg on cultivated land or about 1.7 kg/ha/yr, much lower but geographically rather more uniformly than biological fixation.

(4) Chemical synthesis of nitrogenous fertilizers is an exclusively human contribution to fixation. The primary route of fixation by far is to ammonia, 70% of which is used for fertilizer. The remainder is used for fibers, plastics, and explosives, and never enters the biosphere. Almost exclusively the Haber process and its modifications are used,[8,9] though some ammonia is obtained as a byproduct of coal works.[9] A few percent of fixed nitrogen comes from mining of Chilean saltpeter (potassium nitrate). Fixation uses considerable amounts of increasingly-scarce fossil energy, usually as natural gas, and this is a growing problem (App. C).

Worldwide the total annual production of fixed nitrogen for fertilizer amounted to[4,5] about 40 Tg (million metric tons) in 1975, making it comparable to natural sources. Direct application of ammonia is preferred increasingly, mostly in the developed countries. In the U.S.[7] about 50% of nitrogenous fertilizer is anhydrous ammonia or an aqueous solution thereof. Ammonia is reacted further to yield the other two major forms, ammonium nitrate and urea.

Alone among sources of nitrogen for crops, fertilizer is under direct control by man in the selection of areas and rates of application. Developed countries, which produce[4,5] about 89% and consume about 80% of fertilizer, apply it at an average rate near 80 kg/ha/yr and on individual plots at rates up to 400 kg/ha/yr (as in some U.S. cornfields). This supplies most of the crops' needs, somewhat wastefully; excess inorganic nitrogen washes away or is lost by denitrification (below), little of it simply builds up in soil. Less-developed countries on an average apply fertilizer at a tenth of this rate.

(5) Volcanism injects minor amounts of fresh nitrogen, fixed and elemental, into the atmosphere from the largest reservoir of all, rocks. It is important only on a geological time scale to balance minute losses of fixed nitrogen, washed to the ocean and sedimented.

The relative annual contributions of these five sources to nourishing crops with nitrogen is instructive to compute. Hardy and coworkers[24,30] estimate that biological fixation yields 44 Tg (land covered by legumes 35; rice 4; other crops 5). Abiological sources —lightning, combustion, ozonization— have been estimated above at 2.2 Tg on crop land. Synthetic fertilizers contribute 40 Tg. New fixation on land thus totals about 86 Tg, sufficient to support the growth of 4300 Tg of crops at 2% average content of nitrogen. Annual yields of crops, however, are about 8000 Tg dryweight at *end use*. Initial growth is larger by factors of (i) 1.4 for meat-conversion and spoilage losses, (ii) 5 for total growth/harvested protion, (iii) 2 for losses to insects and disease. The annual growth is thus 1.1×10^5 Tg on cropland. Only 4% of this is supported by new fixation, the rest by decay. It is apparent that decay and assimilation are a tight cycle. Small peripheral losses (below) are compensated by new fixation. While cropland averages the same demand as wild land around the world,[35] intensively-activated land has higher losses (mostly cropping), *and* higher assimilatory demand than biological fixation can provide. Such land needs a larger share of fixed nitrogen from chemical synthates.

Efficiency of use from application to assimilation is the same for all sources but fertilizer, which falls perhaps one-third to one-half lower due to a greater fraction of the losses described below (virtually *all* fertilizer is present as loss-susceptible nitrate).

B. Sinks and Transport Losses

(1) Denitrification[2b,24,36] Various genera of anaerobic soil bacteria derive some of their energy using nitrate as oxidant for carbohydrate, yielding N_2 or nitrous oxide, N_2O . These gases are unassimilable and are lost to the atmosphere. These bacteria are quite universal in distribution. The most favorable conditions for denitrification are low oxygen concentration, presence of actively-reducing compounds, lack of acidity, and high temperatures. Anaerobic conditions favoring the bacteria occur episodically in all agricultural soils (when wet and/or compacted by heavy rains, hard dried, etc.). Anaerobism may even occur concurrently with aerobism, as a mosaic pattern in the soil.[2b] (Anaerobism does not predominate in cultivated areas, or else vascular plants would not thrive.) Low temperatures suppress denitrification, so that losses are mostly concurrent with growth of crops in the warm season. Note that ammonia and organic matter are *not* susceptible to denitrification; conversion to nitrate is necessary. Denitrification is lowered by aerating the soil, actively in tilling or passively by keeping it conditioned with humus and good drainage. On a global basis, the annual amount of denitrification very closely balanced new fixation before intensive agriculture was developed. (Even before intensive agriculture, a lesser proportion of denitrification than fixation occurred on land (*vs* sea)...runoff from land into the sea to the extent of perhaps 15 Tg per year[30] accounted for the extra proportion of denitrifying activity in the sea.) In an average natural ecosystem, denitrification as a sink dominates over runoff/leaching and so nearly matches the average rate of new fixation, perhaps 20-25 kg/ha/yr. On intensively-cultivated land, denitrification is slightly enhanced in absolute rate over natural habitats; there is much more free nitrate in the soil, and the rate of denitrification rises weakly with this concentration.[24] Denitrification as a percentage of the fate of fixed nitrogen added annually in any tilled soil is lower, however. Leaching and runoff are increased in greater proportion, and steady buildup of humus and cropping are new fates for the nitrogen. (Cropped material is consumed, and the waste is disposed of, *off* the land, where it ultimately does denitrify.) I estimate just less than 50% of fixed nitrogen, mostly fertilizer, added annually on intensively cultivated land is denitrified. Most of the remaining 50+% goes to cropping, and lesser

amounts to uncertain proportions of leaching, runoff, and buildup as humus. Because of cropping and humus as extra long-term reserves of nitrogen, denitrification today lags in total rate somewhat behind new fixation worldwide.

(2) Cropping involves removing 20^{+}% of the total plant[37] on the average. In contrast to a natural ecosystem, agriculture almost without exception involves no return of waste from this consumed portion to the land where it grew. The nitrogenous value of the crop as human waste ends up as sewage and landfill in areas remote from cropland, with the minor exception of some sewage used as fertilizer. Cropping can easily exceed total new fixation and impose a continuous loss of fixed nitrogen to exhaustion of all ready reserves; decay of organic matter can supply nitrogen for a long time but at too low a rate for agriculture. Therefore fertilizers are used.

(3) Transport losses. Leaching is the downward percolation of nitrogen compounds, almost exclusively nitrate, dissolved in ground water. It takes nitrate from soil to bedrock or aquifers, out of range of plant roots. It is slow but sure, negligibly affects organic nitrogen (which is insoluble) and ammonia (adsorbed strongly to clays and humus as ammonium ions), and can even dominate the nitrogenous balance of soil in rainy climes. Runoff is a horizontal transport of nitrate or ammonia in surface water from upper layers of soil into streams and lakes, often with the ocean as the ultimate destination. Once in the water, most of the matter is denitrified although some supports growth of photosynthetic plankton including fresh-water algal blooms. Both transport losses occur naturally but have been much increased by human activities: tilling, which causes soil erosion with bulk loss of fixed nitrogen with it; and heavy application of fertilizers which are, or readily become, mobile nitrate far in excess of natural levels. Given that levels of assimilable nitrate are kept as much as five times higher on fertilized land than in similar natural habitats (in the ratio of total yields, roughly) and that tilling increases the fractional loss, the transport losses from fertilized land may be manyfold the natural background. As a fate of added fertilizer, these losses average only a fractional per cent,[38] less than cropping or denitrification. Notably higher losses would have led by now to intolerable widespread nitrate pollution of waters.

(4) Miscellaneous losses include volatilization of nitrogenous compounds. Black[2g] implies that ammonia may volatilize to a noticeable extent from soil,

whereas other workers have found negligible losses in virtually all types of soils.[39] Purely chemical denitrification[2g,24a] by the reaction of ammonia and nitrite may occur, to an unknown and presumably small extent. Michael McElroy of Harvard University and Paul Crutzen of the National Center for Atmospheric Research have recently suggested that such volatilization of nitrogen oxides can cause serious aerial pollution. The National Academy of Sciences will soon release a report.

C. Neutral Interconversion of Forms

Nitrification is the oxidation of ammonia to nitrate by soil microbes.[2e,24,27,36] Aerobic bacteria of the genus *Nitrosomonas* oxidize NH_3 to nitrite, NO_2^- , liberating much energy for their own use. Another aerobic genus, *Nitrobacter*, completes the oxidation to NO_3^- liberating a moderate amount of energy. The maximum energy made available in the overall reaction $NH_3 \rightarrow NO_3^-$ equals the free-energy change; see App. C, Sec. II.A about free energies) of 332 kJ per mole of NH_3 oxidized. It is not captured for the microbes' use with full efficiency, of course.

In even slightly aerated soils — the vast majority — nitrification of ammonia from decay or fertilization is complete in a few weeks or at least in less time than a growing season. Thus plants assimilate most of their nitrogen as nitrate (even legumes...which symbiotically fix only about 25-30% of their needs[40a] directly as amino acids "safe" from nitrification). Plants must reverse nitrification to obtain ammonia for biosynthesis of proteins, chlorophyll, etc. In such reduction they must *expend* at least 332 kJ per mole of NH_3 on thermodynamic grounds, and in practice several times more; see App. B. Thus the 2% of their dry weight present as nitrogen costs them the energy value of about 6% of their final yield. In contrast to other biological processes in soil such as decay, nitrification is performed by a narrow range of organisms and can be suppressed chemically with no untoward ecological effects and with a 10-15% rise in yield of crops (App. C, Sec. IV.A).

D. Assimilation

This is a fairly complex process, even apart from biochemical details ignored here. It is done almost exclusively through the roots (rarely and in small part through the leaves[41] (see App. C, Sec. V.B). The maximum rate at which soil can supply nitrogen to the plant increases with soil reserves of assimilable nitrate and ammonia, and with the mobility of these ions in soil toward the root volume. This rate is often mismatched to (usually lower than) the rate which the plant demands for growing as fast as other nutrients will allow. Over periods of a few days, the gain in assimilated nitrogen should remain in nearly constant proportion to the gain in photosynthesized carbon compounds, providing a "C/N balance."[2a,6a] Chronic undersupply of N can hold back photosynthesis,[2c,42a] which is a simple manifestation of N as limiting the total yield of a plant. Oversupply is not harmful or limiting, except for continued excesses of ammonia (App. B). Excess nitrate can be simply stored internally as nitrate. In other respects, nitrate and ammonia are nearly equivalent in effect. Both are assimilated rapidly and easily.[6] Healthy plants with adequate levels of other nutrients increase growth in response to either.[6] Final yield is, however, about 10-15% higher in the field (also higher in culture, but unmeasured) when ammonia is used exclusively, because the metabolic cost of reducing nitrate to ammonia internally is eliminated (App. B). Such retention of the ammoniacal form in soil requires chemical inhibition of bacterial nitrification, a practical procedure nowadays.

Either assimilable form is usually mobile enough so that virtually *all* reserve within the volume accessed by the roots can be absorbed in a growing season. Extremes of soil pH can decrease this total availability for complicated reasons.[42b] Given a mobilizable reserve, all plants in an area compete, of course. Common weeds' most deleterious effect on crops is their claiming the limited nitrogen supply.

II. AGRICULTURAL MANAGEMENT

One can distinguish five basic agricultural systems, plus a variety of natural ecosystems. Each utilizes the various sources of nitrogen in different proportions, and each may be in steady-state (as is desirable for cropping), declining, or building up soil reserves. The most primitive agricultural system consists of a temporary encounter with a natural ecosystem, diverting it to food crops by the technique of slash-and-burn. The system rapidly declines. A modest crop may assimilate 100 kg/ha/yr of nitrogen, little of which is returned as humus or animal/human wastes. Biological fixation may average 30 kg/ha/yr. Soil reserves of humus are most often large, above 1500 kg/ha, but rate of decay is only 3-4% per year so that in a decade or less the annual yield of crops is poor. More stable agricultural systems involve much more careful, artful balancing of the nitrogen cycle (and other nutrient cycles). Four types of systems are:[43,44] annual crops in tilled soil, which are of most interest here; alternation of annual crops with forage crops; permanent grazing land; and perennial trees or vines. Choice of system is linked to climate and soil on a very local basis. For high yields — giving good economic return and good use of land — all systems require artificial fertilizer. In steady-state their soil reserves of nitrogen will be high, up to 7000 kg/ha.

Most soil nitrogen is reserved in humus, at levels of 1500-1700 kg/ha by area or 0.02-0.4 % (average 0.1 %) by weight[2] distributed preferentially in the fractional meter of topsoil. Assimilable nitrate and ammonia derived from slow decay of this reserve or from new fixation are only a small fraction of this magnitude, not above several hundred kg/ha even with fertilization. Large reserves and high rates of new fixation support a large standing biomass (natural) or heavy cropping (agricultural). Type of soil, type of climate, and type of vegetation all determine reserves and fixation. Stable, drained soil, warm, wet weather, and leguminous plants favor high reserves and fixation. Farmers manage all three factors to some extent — counting irrigation as artificial rainfall — to manage nitrogen, plus other nutrients, of course. High yields infrequently are quite fragile as in some rainy tropics, where leached soils have poor reserves, and the high fixation and very low losses are supported only with natural cover; the system fails drastically under cropping.

Farmers accept certain environmental limitations such as rainfall or temperature by adjusting their choice of crops and at the same time resort to various practices to manage nitrogen and other nutrients. Very complex practices in managing for the highest yield constitute a real art. Direct fertilization is becoming universal as an added source. It is crucial to maintaining intensive cropping. At successively higher rates of application, however, more nitrogen is wasted by increased denitrification or even leaching, or else it is simply tied up in excess humus (App. C, Sec. IV.A). There is no sharp change[2f] in percent utilized with increasing rate of application, so that the "optimum" level must be judged on economic as well as biological grounds. Many other practices work mostly by retarding losses. *Tilling* directs the above-ground residue of plants into humus; aerates the soil to retard denitrification (a gain), promotes useful decay (gain), and promotes nitrification (neutral); but also increases the risk of loss by leaching, runoff, or even erosion. Given reasonably good management, tilling at least conserves the input from other sources (fertilizer, fixation) which counters the loss due to cropping. Careful no-till systems can accomplish all the same results in well-drained soils, however.[13-15] *Irrigation* aims primarily to manage water as a nutrient but may affect nitrogen directly. In rice paddies, algal nitrogen-fixation is supported by standing water. Poorly managed, irrigation can increase anaerobism, cut fixation, and worsen denitrification losses. *Choice of crops* can be beneficial. Legumes can increase soil nitrogen by their moderate amount of symbiotic fixation; since they fix only 25-30% of their own needs, however,[40a] high-percentage cropping as for animal forage can negate or reverse this benefit. As cover for fallow land they provide most benefit and indeed contribute much fixed nitrogen worldwide.[30] Used as intensive crops for human food directly, however, they require and consume fertilizer,[40b] and even decrease their own contribution from symbiotic fixation. Deep-rooted nonlegumes can reduce losses from leaching beyond the upper soil.[45] *Herbicidal control of weeds* is necessary for overall preservation of the metastable,[46] tenuously-balanced ecosystem represented by cropland. It is specifically necessary to prevent diversion of a deceptively-high fraction of assimilable nitrogen into weeds instead of crops. Remedy of extreme *pH* in soil by use of simple acids or alkalis in the fertilizer is necessary in rare instances to keep nitrogen available. Fine-adjustment of pH is done for other reasons.

Use of Fertilizer

Fertilization is almost a uniform practice in all higher-management cultivation and is becoming so in more marginal agriculture in lesser-developed countries. It is crucial to sustaining high yields on intensively-cultivated land such as in Japan where rice may yield 6000 kg/ha, five times the yield of unfertilized fields in Southeast Asia.[1] Monetary gains to the farmer compared to all costs of fertilizer are in a very favorable ratio easily reaching 10-to-1. Synthetic nitrogenous fertilizers account for both major costs and benefits. These fertilizers have about a half-century of history since perfection of the Haber process for making ammonia from nitrogen and hydrogen.

Major chemical forms are anhydrous ammonia or its solutions; urea; and various nitrates, particularly ammonium nitrate. Minor forms include ammonium salts such as the sulfate, and calcium cyanamide. The various forms are broadly equivalent in crop response per unit weight of fixed nitrogen which each contains. Thus a major basis for choice of form is cheapness, convenience of application, and safety to both farmer and crop. Choices are made by type of crop and type of soil/terrain. Ammonia in anhydrous form or solution is cheapest and is now largely preferred.[39] Other benefits of ammoniacal forms are less leaching (until microbial conversion to nitrate occurs during the warm season); nematocidal and fungicidal action; and 10-15% better crop response[2d,47-49] than to nitrates if kept from nitrifying. It creates problems, too, such as chemical hazard to persons; need for some costly equipment; and raising of soil pH, though only temporarily. Ammonia can be toxic to plants but only in concentrations well above practical levels. Other forms such as nitrates and urea are economically competitive in some areas and on some crops; they can be broadcast on the surface simply and cheaply if runoff (and volatization, for urea) is not a problem.

Applied nitrogenous fertilizer is simultaneously assimilated, (nitrified and) denitrified, and leached or lost in runoff. The percentage assimilated we may call the efficiency; it varies with soil and crop, and especially with total amount applied. At the highest levels of application, more weight of fertilizer is assimilated (a motivation for the farmer) but less of the total percentage. That is, denitrification and transport losses increase faster than assimilation. Corn may be fertilized at rates up to 250 kg/ha/yr (400 one year, 100 the next perhaps, for best management), yielding a harvestable portion of 6000 kg/ha/yr of average composition 1% N when wet as harvested. Thus 60 kg of N are recovered from an investment of 250 kg, an efficiency of 24%. A more typical efficiency may be 50% under intensive agriculture, rarely[47] above 75%. Even at inefficiently high levels of fertilization the *incremental* gain in yield may exceed the *incremental* cost of fertilizer in very competitive markets, unfortunately so from the viewpoint of conserving resources and preventing surface-water pollution.[50] Also the efficiency is not a completely straightforward measure, because natural fixation and fertilization are not additive sources. Fertilizer suppresses fixation by free-living microbes (for all crops) and by symbionts (for legumes), when used at any practical level. Further, even the assimilated portion of fertilizer can lead to increased and *un*utilized reserves of humus, in amounts comparable to actual cropping. Total effectiveness of fertilizer is thus lower than the efficiency alone would indicate. Increased efficiency of use calls for (1) less intense competition in markets, which may be achievable in part because most nations have considerable central planning and artificial price structure for agriculture; (2) reliable, quantitative identification of nitrogen sufficiency or deficiency in soil by simple field testing, still an elusive goal;[51,52] and (3) suppression of nitrification of ammoniacal forms with Dow Chemical Company's N-Serve®, which decreases metabolic drain on the plant for assimilation, and decreases denitrification and leaching losses. It gives 10-15% greater yields[47-49] for the same amount of fertilizer or allows the same yield with 10-15% less fertilizer; because most of the yield is the increase due to fertilizer, the efficiency is to 1.1 - 1.15 times that without N-Serve.®

Synthetic fixation of nitrogen is now broadly comparable to natural fixations. Aside from all agricultural benefits and problems the introduction of this large and mobile mass of fixed nitrogen into the biosphere makes for three problems. Two problems arise from eutrophication, the enrichment of various waters by runoff and leaching from cropland. The first problem is the raised concentration of nitrate ion in water consumed by humans and animals. It can reach toxic levels, binding to the blood as reduced nitrite to cause methemoglobinemia.[50,53] Runoff and leaching of a few percent of this nitrate can cause a severe problem locally. The second problem is the long-term imbalance of nitrogen among reservoirs. One might worry that excess nitrate in the ocean leads to excess sedimentation[30] and ultimate loss...or that excess fixed nitrogen in lakes may prematurely age them toward their ultimate fate as meadows. The time scale for ocean sedimentation to be worrisome is tens of millions of years, and the time for damage to larger lakes is only marginally comparable to the brief centuries which mankind has to use resources at today's high rates. The third problem is denitrification of soil nitrates to form volatile nitrogen oxides, which are aerial pollutants. This problem is still under study; see Sec. I.B.5. More pressing than any other problem, then, is the problem addressed in this whole report: the scarcity of energy needed to make fertilizers and sustain today's populations by intensive agriculture.

APPENDIX B

ASSIMILATION OF NITROGEN BY PLANTS: ROUTES, CONTROLS, AND METABOLIC COSTS

I. ROUTES AND CONTROLS

All plants take up ammonia and nitrate at their roots as the predominant means of nitrogen nutrition. Legumes are further able to take up elemental N_2 if one considers the bacteroids as part of them, which is very appropriate metabolically. Some absorption can occur in all plants through the intact leaves but it is minor.[41] Oxidation states other than those represented by NH_3, NO_3^-, and N_2 above are actively toxic, unassimilable, or (like nitrite) present in only minor quantities.

For assimilated nitrate or ammonia, all the internal metabolism is the same beyond the internal stage of ammonia, to which nitrate is brought by a metabolic effort. Legumes can accept additional input to metabolism at one stage beyond, namely, amino acids from the bacteroids, but only for 25-30% of their total[40a] fixed nitrogen. The rest comes in as soil nitrate or ammonia as in other plants. This additional input of amino acids is subject to different control mechanisms and is sensitive to other environmental factors (temperature, chemical concentrations) than is the assimilation of nitrate or ammonia. The metabolic expenditure between the stages of ammonia and amino acids, however, is only minor.

The first step in assimilation of any form of nitrogen is clearly transport across the outer, plasma membrane of root cells. As for any other solutes there are several conceivable molecular mechanisms to achieve this transport[42c] -- diffusion, facilitated diffusion, active transport, etc. The mechanisms of transport are only a peripheral concern here, because (1) major metabolic costs of reaching the ammoniacal stage arise not in transport but in the internal reduction of nitrate or fixation of N_2; (2) controls over the amounts of NH_3, NO_3^-, or N_2 assimilated can be described phenomenologically as "black boxes," when one is interested only in final rates of assimilation and is not contemplating — as one *is* for nitrogen fixation — any chemical or genetic changes in mechanisms of assimilation.

A. General Controls

There is a preferential ranking of nitrogen-sources. When both are present, ammonia is assimilated preferentially over nitrate.[6b] Legumes favor assimilation of either over nitrogen fixation[33a]...even though metabolic costs of reducing nitrate very nearly match costs of fixation. However, toward the time of fruiting, nitrogen fixation becomes dominant and progressively shuts off assimilation of nitrate or ammonia.[54]

In response to nitrogen-deficiency, plants curtail some activities such as synthesis of protein and leaf growth. Ultimately even resistance to diseases is much affected.[2h] Perhaps as a form of "hoarding" for times of nitrogen-stress, plants can assimilate both soil forms, nitrate and ammonia, beyond immediate needs. Nitrate may accumulate as such, and it may also be reduced to ammonia with moderate speed if the plant is preconditioned to do so. Such over-assimilation possibly leads[2i,6b,55] to a depletion of carbohydrates by diversion to proteins; to excess succulence and structural weakness; and to delaying of maturity in favor of a longer period of vegetative growth. Ammonia always presents this hazard, nitrate does so only if it is rapidly reduced instead of accumulated. Thus the nitrate form which predominates naturally is a lesser hazard to the plant's carbon-nitrogen balance. Reduction of nitrate is favored by high levels of the enzyme nitrate reductase, either constitutive (genetically programmed to be continuously at high levels, as in species of maize) or induced by a previous history of exposure to much nitrate.[56a] The herbicide Simazine kills fast-growing weeds by inducing high levels of reductase, specifically by retarding its normal breakdown and recycling.[42d] Only very rapid photosynthesis of carbohydrates can protect against this hazard of imbalance. Maize, a super-efficient "C_4" plant (App. C, Sec. V.E) is so protected in general. Other plants are susceptible, particularly during slow growth in the dark or during early growth.[6a] Interestingly, nitrogen fixation as a third route of assimilation in legumes does not function to excess and threaten the carbon-nitrogen balance.

B. Uptake and Reduction of Nitrate

Uptake[6c,42b] depends upon the soil pH and is optimum in acid soil near pH 4. In turn, assimilation alters the pH, raising it toward alkalinity, especially very near the roots. Nitrate may accumulate internally, which is harmless to the plant but toxic to some animals that may eat it. Abnormally large accumulation can occur when the plant is deficient in molybdenum[42e] and thus cannot make enough nitrate reductase. Nitrate may amount to 10-15% of total dry weight under such conditions! Normally, nitrate is much lower in concentration but still variable, decreasing particularly with the cumulative exposure to sunlight during the day and with increased availability of water.[57a]

Reduction of assimilated nitrate is all enzymatic[58] and occurs in at least two steps, $NO_3^- \rightarrow NO_2^-$ and $NO_2^- \rightarrow NH_3$. Nitrite, NO_2^- , never accumulates significantly.[59a] Much is known about the entire scheme of reduction.[42g] There are enzymatically-bound distinct intermediates between NO_2^- and NH_3 which amount to additions of successive pairs of electrons and achieve oxidation states +1 , -1 . The refractory 0 state, N_2 , is skipped.

Both light-dependent and light-independent "dark" mechanisms of reducing NO_3^- and NO_2^- are known,[42g] including more than one dark mechanism for $NO_2^- \rightarrow NH_3$. Reduction can also be generally sensitive to light not used directly for chemical reducing power but for synthesis of nitrate reductase itself.[56a] All mechanisms consume notable amounts of energy, of course, to generate chemical reducing power. Both roots and leaves reduce for NO_3^- and NO_2^- , by dark and light mechanisms, respectively. The relative percentage of reduction done by leaves and roots varies with species of plant.

There are also paths of reduction that are "dissimilatory", leading to loss of nitrogen as N_2O or N_2 instead of its ultimate assimilation into amino acids. Nitrate respiration[42h] is the oxidation of carbohydrate by nitrate instead of oxygen. It is well established in bacteria but less surely for higher plants, where it is probably negligible except in molybdenum-deficiency. Also, chloroplasts in leaves show ability to perform a small part of the reduction of both NO_3^- and NO_2^- within the very organelle[60] but on an ill-defined metabolic path not leading to amino acids.

C. Uptake of Ammonia

Uptake[6c,39] also depends upon pH as it does for nitrate, while the optimum is in neutral or slightly alkaline soils. Uptake lowers the soil pH, faster than nitrate uptake *raises* it for the same total amount of nitrogen. Ammonia never accumulates internally but is rapidly incorporated into protein by enzymes that are never deficient.

D. Fixation of N_2 by Internal Root Symbionts

This is described in some detail in App. C, Sec. V and in Ref. 28 among other books. The initial stage of root infection is retarded by acidity of the soil and several other factors.[33] Availability of elemental N_2 in the soil is never presumed to limit fixation, whereas internal metabolism *is* limiting.

II. METABOLIC COSTS OF INCORPORATING NITROGEN, AS A FRACTION OF FINAL YIELD

The major metabolic costs of getting soil nitrogen (NO_3^- , NH_3 or N_2) into the plant at the universal stage of NH_3 (or amino acids) are in reduction of nitrate or of N_2 (fixation), and not in initial transport of soil forms across the plant membranes. Therefore in assessing costs to the plant I assign the assimilation of soil NH_3 as costing nothing, and NO_3^- or N_2 as costing only for their enzymatic reductions.

A. Cost of Reducing Nitrate to Ammonia

A plant is initially supplied with the inorganic compounds water, CO_2 , NO_3^- , etc., at nominally fixed concentrations. To synthesize NH_3 from these the plant must expend energy, ultimately derived from sunlight and delivered to the synthesizing (reducing) enzymes as the intermediate carrier, carbohydrate. The minimum energy needed for the reduction reaction is calculable from the thermodynamic change in free energy for the reaction

$$HNO_3(\text{aqueous}) + H_2O(\ell) \rightarrow \underline{\underline{NH_3}}(\text{aqueous}) + 2O_2(g), \qquad \Delta G^0 \simeq +300 \text{ kJ/mole } NH_3.$$

(Concentrations of reactants and products differing from 'standard states' alter ΔG but by a relatively minor amount. Also, oxygen gas, O_2, is not liberated by plants as an end product; however, the oxidant that is liberated and used immediately is equivalent to atmospheric O_2 which may be considered "costless" and "gainless.")

I will consider carbohydrate as the primary source of energy, representing in its formation from CO_2 and water a free energy reserve of 3040 kJ/mole glucose (= $C_6H_{12}O_6$, 180 grams) or 16.9 kJ/g of glucose. From the ultimate source of energy = sunlight, glucose is formed with notably less than 100% efficiency, but this inefficiency is shared by *all* processes in the plant, which all tap photosynthesized carbohydrate (cH). Besides, cH represents the bulk of the net yield of any plant grown and thus is a good base for energy accounting.

(1) Internal economy. Minchin and Pate[61] note a requirement of 6.2 mg carbon or 15.5 mg carbohydrate (say, glucose) per mg of N as NO_3^- reduced to NH_3 (and incorporated in proteins). This cH is respired or oxidized to $CO_2 + H_2O$ to supply energy for the enzymatic reduction and for synthesis of the enzymes themselves. It is also incorporated as the carbonaceous part of proteins. Only the former uses of cH represent a *loss of dry-weight yield* to the plant, the quantity I wish to calculate. The authors do not quote percentages

of total cH going to each of the end uses above as they did for fixation, but I can estimate these. Because the metabolism from NH_3 to amino acids is the same in nitrate reduction and fixation, the amount of cH re-exported as the carbonaceous part of proteins should be the same, namely, 53.2 mg carbon per 25.5 mg N given to the aerial parts of the plant (their Table 3), or 2.1 mg carbon/mg N = 5.25 mg cH/mg N . The rest, (15.5 - 5.25)mg cH/mg N , is respired and lost. Thus each milligram of finally fixed N in the plant costs about 10 mg of cH. Now, out of each 100 mg of dry material of the plant 2 mg on the average is N . This dry material can be well approximated as 98% cH plus 2% N . Initial synthesis of 118 mg cH would allow 98 mg cH to remain and 20 mg to be lost in order to gain the 2 mg N . (This presumes that later resynthesis of both cH and protein from whatever initial sources during the life of the plant is negligible, which is quite false.) Thus, acquiring its 2% of weight of fixed N would cost the plant 20% of its yield, compared to acquiring N as already- reduced NH_3 . This 20% figure is high compared to field tests of nitrate versus ammonia...by a factor of about 3 as I guess below. Therefore, one may judge that (a) the cost of resynthesis of (cH and) protein from already assimilated materials is about twice the cost of initial synthesis, and (b) in any event, initial reduction of NO_3^- is costly...perhaps 6% of *final* yield.

(2) Field tests. Ordinarily, plants get their nitrogen from soil nitrate. When the source is soil ammonia which is kept as such (prevented from nitrifying with the chemical N-Serve®), yields rise 10-15% for the same amount of nitrogen supplied.[47-49] I will assume an average of 12% increase. Some increase is no doubt due to more of the fertilizer remaining in soil, because less ammonia than nitrate is lost to leaching and runoff. Another portion of the increase is as surely due to the metabolic costlessness of using NH_3 compared to NO_3^- . I arbitrarily assume that the two contributions to the increase are equal, in the absence of any experimental tests—which should be done. Thus, initial reduction of $NO_3^- \rightarrow NH_3$ may cost the plant 6% of its final yield. This is the origin of the figure I used in part (1) above for a plausibility argument.

(3) Is fossil energy used to synthesize NH_3 fully wasted when it becomes nitrate? No; nitrate-reduction is only about 10% of a plant's energy budget. Increasing the availability of nitrogen is a more "catalytic" use of energy. Loss of the NH_3 energy is not crucial as long as extra nitrogen in

some form remains available. By removing a limitation to growth, much better use of the larger "pool" of solar energy for growth is possible. Gain in solar energy fixed because N is available exceeds the expenditure of fossil energy in making fertilizer, by perhaps 7:1.

B. Cost of Fixing Elemental N_2 to Ammonia

The concepts just discussed apply here, too. Now the reaction is

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2O(\ell) \rightarrow NH_3(\text{aqueous}) + \frac{3}{4}O_2(g) \;,$$

with virtually the same ΔG^0 (8 kJ/mole NH_3 less).

(1) Internal economy. Minchin and Pate[61] also performed very detailed investigations of the metabolic costs for fixing of nitrogen by root nodules in legumes. The total consumption of cH was 5.9 mg carbon = 15.8 mg cH per mg N_2 fixed as NH_3. Of this 15.8 mg cH, 5.25 mg was returned as the carbonaceous skeleton in amino acids re-exported by root nodules, such that about 10.5 mg cH were either (a) respired and lost to support growth and enzymatic reactions, or (b) incorporated into the extra root tissue needed for the nodules...which is a loss to the above-ground harvestable crop anyway. This figure of 10.5 mg cH/mg N fixed very nearly matches the 10.0 mg cH/mg N for NO_3^- incorporation. Therefore I conclude that nitrogen fixation also costs the plant about 6% of its final yield. (This final yield is lower for legumes on a per-hectare basis compared to average non-legumes, but this is a genetically-set limitation on initial energy captured by photosynthesis, such that cH-synthesis and N-assimilation down the line from photosynthesis are equally affected.)

(2) Field tests of nitrogen-fixation's costs to yield are not available. However, it is known that grain legumes do not respond well to being supplied with NO_3^- instead of letting them fix N_2. This is rationalized as follows: (a) NO_3^- costs as much metabolic energy as N_2, so fertilization does not reduce the energy burden; (b) though other plants bear the burden of NO_3^--reduction while increasing yield dramatically when supplied with NO_3^-, they can do so because their basic supply of photosynthetically-captured energy increases with nitrogen-availability. Grain legumes are presumably limited in photosynthetic capacity by inborn metabolic peculiarities unrelated to nitrogen-stress.[40a]

(3) Inherent Inefficiencies in Fixing N_2 Symbiotically. Net fixation expends the energy in 10 mg cH per mg N fixed, or 2370 kJ/mole NH_3. Since the theoretical minimum is 300 kJ/mole, efficiency is 13%. In practice, fixation requires hydrogen, which respiration of cH generates as a high-energy reductant (H), more powerfully reducing than H_2. Even though the $H_2 + N_2$ reaction is already *downhill*, extra energy (12-15 ATP's per NH_3) is provided to the enzyme to *activate* the reactants. (H) is made at perhaps 60% efficiency from cH, and ATP at 35% efficiency. Thus, the main biosynthetic reactions are about 50% efficient. A side reaction generating useless H_2 from (H) wastes about 40% of the input energy, giving a net 30% biochemical efficiency. The need to make and maintain the enzymes and all associated tissues brings whole-plant efficiency down to 13%.

APPENDIX C

STRATEGIES FOR IMPROVING WORLD-WIDE NITROGEN-NUTRITION OF CROPS AND USE OF CROPS

I. CONTEXT OF THE STRATEGIES

Growing enough food for a burgeoning population is clearly a major international problem. The straightforward approach to this problem is simply to grow more food crops with the developable resources of land, water, fossil fuels, labor and capital. [I will generally ignore other and equally-necessary approaches such as stabilizing world population, or using agricultural/ silvicultural products in new, nonfood ways. These are mentioned if directly relevant to nitrogen-nutrition.] A very effective strategy within this general approach has been improving the nitrogen-nutrition of crops, especially by expanding the use of synthetic nitrogenous fertilizers which yield a handsome return in dollars and in resources. However, the manufacture of ammonia specifically for such fertilizers requires a somewhat alarming fraction of our dwindling fossil fuels: 1.2-2.0% of natural gas, and 0.4-0.7% of total energy in the U.S.[11,12] The total strategy has more options and is more hopeful: manufacture more fertilizer, by traditional or radical technologies; optimize the use of nitrogen-sources by any species of plant, as by reducing losses of applied nitrogen from the soil; open new routes for biological fixation of nitrogen, as by finding new symbiotic bacteria for crops lacking any; utilize crops for food more effectively, by choosing the most efficient crops or by using the protein in leaves.

In the next decade this strategy will be implemented in its various parts by enterprises and nations. Large commitments of capital, labor (including research and development), and natural resources must be made. Decisions must be made in three areas of policy: (1) *Economic development*. How shall available technologies, labor,and other resources be committed, such as: Shall the major investment continue to be the building of more Haber-process plants for ammonia, given their costliness and the limited future of hydrocarbon fuels which they now require? [The answer is a definite "yes," especially if conservation of energy in the whole economy is implemented.] (2) *Technological development*. What new technologies shown to be sound scientifically in limited circumstances are also sound economically on a large scale and deserve to be developed, such as: Shall fermentation of crop residues to methane be pursued? [Yes, in units built for single farms.] (3) *Scientific Research*. How large an effort is warranted to answer scientific questions about a specific technology, such as: What are rates of reactions in proposed schemes for thermochemically decomposing water to yield hydrogen for the Haber process?... Or to answer basic questions, such as: How does the nitrogen-fixing enzyme nitrogenase function?

This Appendix describes each of 16 strategies to improve nitrogen-nutrition, which vary in extent of application, degree of development, and need for further research. I present for each strategy key concepts; quantitative economic and scientific constraints (e.g., production of hydrogen by electrolysis of water will always take more energy than production by "reforming" natural gas) bearing on ultimate practicality; and research needs and the hope one might have in overcoming obstacles in research — such as finding a new low-temperature catalyst for the process.

II. APPROACH ONE. FIX MORE NITROGEN INTO AMMONIA BY CONVENTIONAL CHEMISTRY

Most ammonia today[8,9] is manufactured by direct chemical combination of nitrogen and hydrogen ($N_2 + 3H_2 \rightarrow 2NH_3$) with heat (400 up to 650°C), pressure, and catalysts used to favor or speed the process. Collectively we may include all variations such as Claude-Casale under the title of "Haber process." Clearly, the process requires sources of H_2 and N_2, a catalyst, and apparatus for heat/pressure generation and containment. Hydrogen and heat are both provided by fossil fuels, primarily natural gas which is essentially methane (CH_4) . Cost of the process is dominated by cost of fossil fuels, particularly in generating hydrogen;[64a] followed by costs of compression;[9] and then by capital equipment. Hydrogen is made from methane by the "reforming" reaction (1) below. Heat from the combustion reaction (2) is used to drive reaction (1), which is "uphill" in energy. The heat also is used (in principle, recoverably) to speed the rate of the final synthesis (3).

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{1}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{2}$$

$$3H_2 + N_2 \rightarrow 2NH_3 \quad . \tag{3}$$

The process has more complex details, of course. Reaction (2) often is used to provide N_2 as well from air; products of both reactions must be "cleaned up;" etc. Gross annual production worldwide is about 50 million metric tons (Tg),[4] at an average production cost of \$0.094/kg (3.8¢/lb) of NH_3, of which perhaps 80% is attributable to the cost of natural gas. Energy-efficiency of production, based on the amount of gas consumed compared to the thermodynamic minimum, is a respectable 54% as will be shown.

A. Resource Costs

We may calculate the minimum consumption of methane on thermodynamic grounds. The stoichiometry or mix of reactions (1) and (3) required to produce one mole of ammonia is $\frac{3}{8} : \frac{1}{2}$,

$$\begin{array}{lll} & \frac{3}{8}\,[CH_4(g) + 2H_2O(\ell) \rightarrow CO_2(g) + 4H_2(g)] & \text{yields } \frac{3}{2}\,H_2(g) \\ + & \frac{1}{2}\,[3H_2(g) + N_2(g) \rightarrow 2NH_3(g)] & \text{uses } \frac{3}{2}\,H_2(g) \\ \hline \end{array}$$

$$\text{Net:}\quad \frac{3}{8}\,CH_4(g) + \frac{3}{4}\,H_2O(\ell) + \frac{1}{2}\,N_2(g) \rightarrow \frac{3}{8}\,CO_2(g) + \underline{NH_3(g)} \quad . \tag{1⊕3}$$

Physical states are noted parenthetically as gas (g), liquid (ℓ). How much driving force is needed for net reaction (1⊕3), or how endoergic is it? Two accounting methods are useful:[65] free energy changes ΔG in reactions, and perhaps-more-tangible enthalpy or heat changes ΔH . Free energy is useful for all kinds of energy sources (electrochemical, thermal = combustive, compressive, etc.) and is preferred. The change ΔG depends upon initial and final concentrations as well as species (it is easier to make ammonia when little has accumulated than when a lot is present). Because the concentration factor is often relatively small, I shall employ[66] so-called standard-state values ΔG^o between fixed concentrations of reactants and products. Values of ΔG^o for reactions (1) and (3) are respectively 130.98 kJ/mole and -32.68 kJ/mole. Thus the balanced net reaction $(1\oplus 3)$ is endoergic by +32.76 kJ per mole of NH_3 . The combustion reaction (2),

$$[CH_4(g) + 3O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)],$$

liberates -819.14 kJ of free energy per mole of CH_4 ; thus 32.76/819.14 = 0.040 moles of CH_4 combusted could drive the reaction $(1\oplus 3)$. Minimal net consumption of CH_4 is (3/8 + 0.040 = 0.415) moles per mole NH_3 . On an enthalpy basis, reaction $(1\oplus 3)$ consumes +49.11 kJ/mole and reaction (2) provides -891.63 kJ/mole CH_4 , such that 0.055 moles of CH_4 are needed in reaction (2) if only ΔH is recoverable. The minimal net consumption is then 3/8 + 0.055 = 0.430 moles CH_4/mole NH_3 , very similar to the above. (Both minima are increased very slightly if combustion is postulated practically to yield gaseous water *vs* liquid water, yielding less useful energy.) Actual methane consumption[10] is 36,000-40,000 SCF (standard cubic feet at 60°F) per metric ton of NH_3 , or 43,200-48,000 moles CH_4 per 58,800 moles NH_3, an average 0.776 moles CH_4/mole NH_3 . *Molar efficiency* in use of methane is then (0.415/0.776) x 100% = 54% . We may call this an efficiency of using fossil energy as well. This is a respectably high value for a process driven at a usably fast rate. Compare 33% for electrical power generation[67] and 77% on a ΔG^o- basis for commercial electrolysis of water.[68] Most of the losses occur in heat transfer from reactions (2) to $(1\oplus 3)$, and in gaseous compression-decompression and heat-cool cycles. $H_2 + N_2$ are compressed and heated repetitively in most variants of the Haber process because conversion to NH_3 is only 8-40% on any one pass.[8,9] Furthermore, some valuable H_2 is lost by incompleteness of recycling; usually some gas is "bled off" during each cycle to avoid buildup of inert gases. At quite lower temperatures, conversion per pass would be greater, fewer passes would be needed, and bleed-off losses and heating/compression costs would be lower. Net energy efficiency might be 5% better, to 59%. However, no low-temperature catalysts have been successful as yet.[11a,64b]

B. Possible Improvements of the Haber Process

Clearly, the shortage of fossil fuels threatens the continued use of the Haber process. Barring the timely perfection of fully substitutional strategies of nitrogen-nutrition (see esp. Two.A and Four. A through Four.F), the threat extends to intensive agriculture and thus to world food supply. (Crop yields sufficient to support the world's population are insupportable with present agriculture and technology, minus fertilizer.) The Haber process, strictly defined as the synthesis $N_2 + 3H_2 \rightarrow 2NH_3$, admits of relatively minor improvement in efficiency (the low-temperature catalyst), hence of improvement in stretching resources. Conscientious conservation in the total use of energy by the developed countries, especially the U.S. which uses the most energy per capita, and per unit of gross national product, would give much more elasticity[69] to supplies of fossil fuels. A second broad route for saving the Haber process is finding new sources of hydrogen. I discuss possible sources as separate strategies Two. B, Two. D later in detail, but it is not redundant to discuss right now the broad limits on improving the availability of hydrogen.

Methane yields hydrogen plus additional thermodynamic driving force (via combustion) for the Haber process with *ca* 54% efficiency in energy. Because all energy used in the Haber process (for combustion, compression, etc; and whether or not derived from methane) competes in other markets, the energy-efficiency of alternate routes should also be high. Let us consider constraints on efficiency for deriving hydrogen from water without fossil fuels. The net synthesis of ammonia from nitrogen and water,

$$\frac{1}{2}\,N_2(g) + \frac{3}{2}\,H_2O(\ell) \rightarrow NH_3(g) + \frac{3}{4}\,O_2(g) \quad , \qquad (4)$$

consumes a minimum energy $\Delta G^o = +339.9$ kJ. As noted earlier, 0.415 mole of methane can supply this energy at perfect efficiency. Add to (4) the reaction below, for its value as energy only,

$$(3/8 + 0.040)[CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)] ,$$

to get reaction $1 \oplus 2 \oplus 3$. The primary source of energy alternative to fossil fuels is nuclear fission. Nuclear energy is never used directly in any industrial process, but as electricity instead. Electrolysis of water to hydrogen is quite feasible in itself, being 77% efficient in using energy to drive the reaction

$$H_2O(\ell) \rightarrow H_2(g) + \frac{1}{2} O_2(g), \quad \Delta G^o = +235.8 \text{ kJ} ,$$

in present commercial practice; other losses[70] *en route* to ammonia should be just the same as with reforming. However, efficiency from nuclear energy to electricity is only 0.315 on the average,[67] implying a net efficiency[70] for synthesizing ammonia of perhaps 20%. (Even though at present nuclear energy is never used directly, it is fair to compare it to fossil fuel regarding efficiency from raw energy to end use. Later uses of nuclear energy may be more direct, and for the same end use, electricity, the dollar costs of nuclear and fossil energy are quite close.) In all, one would expect replacement of methane by nuclear-electric energy to more than double the cost of ammonia.

Direct use of raw heat from a nuclear reactor to decompose water is envisioned in thermochemical schemes (strategy Two.C below) with projected efficiencies of 50%. Net efficiency for making NH_3 by reaction (4) is then estimated, by calculations similar to those in Ref. 70, to be 38% — rather near competitiveness with reforming of methane. Use of hydrogen made by gasifying coal with water (Two.B) may be even more competitive.

C. Prospects for the Haber Process

(1) In the next 10-20 years, one may expect only minor gains in the efficiency of making ammonia by reforming of methane coupled to the Haber process, from 54% → *ca* 60%... if and when new low-temperature catalysts[11] are developed. These catalysts must be comparable in throughput to old ones, stable, cheap to make, and cheap to recycle chemically if necessary.

(2) Full replacement of the reforming/Haber (r/H) process is at least 50 years away. Finding enough fossil fuels or sources of hydrogen for this process over this period is crucial.

(3) The r/H industry will expand despite rising costs, because food prices will rise about as fast due to nonfertilizer costs (land, water, labor...), thereby keeping the cost:benefit ratio for fertilizer sufficiently

low. Thus the r/H process will retain or increase its fractional use of ever-scarcer fossil fuels, for economic reasons.

(4) Fossil fuel used for the r/H process will be slightly decreased in use in other sectors of the world economy. This will lessen the economic pressure on the r/H process. Conservation intensive enough to "save" the Haber process and other critical manufacturing for a crucial 50 years may require active governmental intervention such as energy rationing. This is certainly true for countries lacking appreciable reserves of coal. In coal-rich countries (Russia, U.S. principally), gasifying coal + water to hydrogen could support the Haber process for centuries if perfected. Use would be local and captive, since H_2 is costly to ship. Coal-rich countries would monopolize the manufacture and sale of ammonia, therefore aggravating some political tensions. A complicated task demands doing, namely, projecting attainable levels of manufacturing ammonia. Will ammonia at bearable prices last long enough to contain the threat of famine for a half-century, given that population will not stabilize until later?

(5) The r/H industry *per se* shows a disturbing trend[5] toward keeping an increasing fraction of its output *vs* exporting it. The two direct causes are increasing internal consumption by industrialized countries where most r/H plants are located, and poor performance of plants in the less-developed countries. Thus the countries with greatest need suffer relatively. The ultimate causes are not technical problems, but sociopolitical ones.

(a) Developed countries (DC's) tend to exploit a far greater share of natural resources in LDC's than do the LDC's themselves. The DC's are motivated by the desire to keep a positive balance of trade easily. Only the oil-producing LDC's have reversed the role. For largely economic reasons, DC's tend to give ineffective technological aid to LDC's with less valuable resources. Another reason, to be sure, is that varied industries must develop together to survive, a very expensive prospect.

(b) LDC's insufficiently appreciate their technological problems. Their political leaders draw upon a narrower group of informed advisers than do leaders in DC's, and hence often confuse the boundary between technological and political problems. Socioeconomic structures are also not geared to stabilizing population while improving production, especially of food. Thus, gains are largely cancelled. (Consider the "Green Revolution," which advanced rich farmers selectively over poor ones.[1] The poor must still rely on having many children for economic security.) In all, the trend noted above contributes to destabilizing world government, indirectly threatening world food supply, which forms our ultimate concern.

(6) The output, ammonia, will be conserved by use of better methods and lower gross levels of fertilization. Strategies of type Three below must be implemented worldwide: accurate testing for excess soil nitrogen; increasing retention of soil nitrogen and decreasing metabolic costs of assimilation to the crop, by suppressing nitrification of $NH_3 \rightarrow NO_3^-$; and ensuring that ammonia is not lost by use of substandard field-application equipment.

(7) In a crisis over energy, severe enough to drastically limit energy available to agriculture, manufacture of fertilizer from ammonia is more expedient to retain than heavy mechanization and energy-intensive food-processing. The fossil-fuel "subsidy" to agriculture[14] in the U.S. (a "worst case") in 1974 was 2.6% of total U.S. energy, and total subsidy on- and off-farm to food including transportation, processing, and marketing is three times this.[71] Given the labor attendant to all activities (including that fraction of the petroleum and machinery industries dedicated to agricultural use perhaps 20% of the U.S. labor force[72] is dedicated to food...*vs* 5% on the farm alone. Cutting energy use off-farm is clearly a prime target, e.g., marketing crops over smaller areas, or processing food less. Economic disruption would be concentrated on so-called middlemen.

Cutting energy use on-farm is feasible, too. Fertilizer[14] accounts for 27% of the use on-farm (87% of this[11] in turn for nitrogenous fertilizers), whereas gasoline for machinery accounts for 40%. Replacing machinery with labor would be more an unmasking of labor-intensiveness (above) than a real increase of same. Furthermore, less tilling might improve yields. See Strategy Three. A.

(8) Continuing heavy use of nitrogenous fertilizers demands that we solve problems of (a) nitrate pollution in ground water and surface water, (b) NO_x pollution by volatilization from soil. Magnitudes of problems are being assessed in the U.S. in studies sponsored by the National Academy of Sciences; see App. A, Sec. I.B.5. Optimal usage of fertilizers as in point (6) above alleviates the problem. In particular, suppression of nitrification by applying the chemical N-Serve® keeps ammoniacal fertilizer in the soil- bound ammoniacal form, in addition to lowering total need in other ways. Rotation

of crops including deep-rooted ones such as alfalfa also helps, by assimilating nitrogen that leaches beyond normal root zones.[45]

(9) Keeping intensive cultivation *per se* will require this minimal expenditure of fossil energy for fertilizers. The alternative of "organic farming" is not viable. It would require too much land due to lower yields per area; the loss in natural habitats alone would be excessive, even if enough land *could* be found.

III. APPROACH TWO. FIX NITROGEN BY RADICAL TECHNOLOGIES THAT REPLACE ALL OR PART OF THE REFORMING/HABER PROCESS

A. Direct Oxidation

The twin barriers of nitrogen's unreactivity and unavailability to plants can also be breached by forming its oxides. Nitric oxide (NO) in particular is a common intermediate in the synthesis of nitrates and nitric acid. Commonly, NO is made by oxidizing ammonia -- a roundabout tour in oxidation state from zero (N_2) to $-3(NH_3)$ to +1 (NO), which is, however, favored kinetically[25a] over direct oxidation $N_2 + O_2 \rightarrow 2NO$. Direct oxidation all the way to nitric acid is almost thermoneutral or costless at theoretical minimum,

$$\frac{1}{2}N_2(g) + \frac{1}{2}H_2O(\ell) + \frac{5}{4}O_2(g) \rightarrow HNO_3(\text{aqueous}), \qquad \Delta G^o = +8.09 \text{ kJ/mole},$$

whereas the intermediate formation of ammonia is costly uphill. Even though the follow-up transformation to nitric acid is downhill,

$$NH_3(g) + 2O_2(g) \rightarrow HNO_3(aq) + H_2O(\ell)\ , \qquad \Delta G^o = -331.8 \text{ kJ/mole},$$

the energy liberated is not applied in practice to driving the uphill formation of ammonia [$\Delta G^o = +339.9$ kJ/mole, reaction (4)]. (This inability to recover a significant portion of the energy liberated by a downhill step to apply to an uphill step is extremely common, and is in some ways analogous to "braking" a vehicle downhill to remain in control, sacrificing ability to roll up the next hill. Reactions when performed electrochemically are more amenable to being coupled, but the apparatus is expensive and the rates are hard to match to each other.)

In direct oxidation, the intermediate NO lies at a high free energy, unfortunately,

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g) \quad , \qquad \Delta G^o = +86.8 \text{ kJ/mole} .$$

The kinetics are also unfavorable, in part because there are no stable intermediates between N_2/O_2 mixtures and NO . High temperatures can be used but then the decomposition backward to $N_2 + O_2$ is also rapid. Rapid quenching to lower temperatures in less than a few milliseconds is employed, rather wastefully of energy (an additional 18.4 kJ/mole is expended at each quench from 2200 C to the safe point 1000 C, 50 times over because conversion is only 2% per heating). Low-temperature electrical ionization forms a yet-higher intermediate, the N_2^+ ion at 750 kJ per 1/2 mole N_2 , but has a typically higher efficiency of 25%. Therefore, synthesis of NO would realistically consume 3000 kJ/mole NO in electrical energy, derived in turn from 8600 kJ of fossil fuel energy converted to electricity with 35% efficiency.[67] Compare this to the Haber process for ammonia, consuming 0.776 moles CH_4 per mole NH_3, equivalent to 636 kJ/mole NH_3 . Because of this 14-fold discrepancy in cost of fuel, direct-oxidation manufacturing plants have been demonstrated but never have been successful commercially.[8a,9a]

Prospects: None

A few people[64,73] have speculated on the use of cheaper sources of ionizing energy to drive direct oxidation of N_2 . Raw fission energy inside a nuclear reactor of proper design might be 25% efficient at causing oxidation. Energy required is thus as above, but it is available at considerably less dollar cost than output electrical energy or equivalent fossil energy.[64] However, this and any other schemes using cheap, raw energy of fission or fusion have two drawbacks, the second one being insuperable. (1) They divert energy resources otherwise useful at higher efficiencies; although saving dollar costs immediately, they squander resources to raise costs later. (2) Fission products in a reactor of the design contemplated in Ref. 73 cause extreme radioactive contamination which can never be removed to acceptable residual levels in economical fashion. Fission/fusion could be used in underground explosions[64] for indirect thermal formation of NO or NH_3 . Contamination might be nearly tolerable, but ground shocks and costs are not acceptable considering the experience with natural gas recovery.[74]

Prospects: None

B. Gasification of Coal + Water to Hydrogen

Section II.B earlier developed the concept that the Haber process could be continued economically if new sources of hydrogen (H_2) were developed to replace hydrocarbon-fuel reforming. Coal is a fossil resource of much greater extent than hydrocarbon fuels but is not a direct replacement in the reforming apparatus for generating hydrogen. There is a great similarity in the net reactions:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2$$

However, the balance of CO_2 to H_2 is different, which defeats the fine adjustments in the chemical engineering of a reforming plant.

Thus the Tennessee Valley Authority in the U.S. (D. Waitzman, project manager) is contracting for development of a gasification process which will match the product composition from natural gas reforming. "Reforming", previously used herein to denote the net reaction, is now taken as the first step only,

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad ,$$

which is followed by "shift conversion"

$$CO + H_2O \rightarrow CO_2 + H_2 \quad .$$

For coal, the initial gasification

$$C + H_2O \rightarrow CO + H_2$$

could be followed by a *partial* shift conversion with removal of the CO_2 formed:

$$C + H_2O \rightarrow CO + H_2 \begin{cases} \longrightarrow CO + H_2 & (1/2) \\ \xrightarrow[+ H_2O]{} \underset{\text{remove}}{\cancel{CO}_2} + 2H_2 & (1/2) \end{cases}$$

$$\overline{1/2 \; CO + 3/2 \; H_2}$$

The same ratio of $CO:H_2$ is achieved as in reforming. The entire process would involve additional fine adjustments, such as partial desulfurization.

(1) This process is not perfected or demonstrated yet. However, it is expected to have fewer technical difficulties than coal gasification to methane for general use, which is the object of much research and development. This "methanation" is the more difficult sequence of reactions

$$\begin{array}{lcl} C + 2H_2O \rightarrow CO_2 + \underline{2H_2} & & \text{(reforming + shift conversion)} \\ C + \underline{H_2O} \rightarrow \underline{CO} + \underline{H_2} & & \\ \underline{CO} + \underline{3H_2} \rightarrow CH_4 + \underline{H_2O} & & \text{(inverse shift conversion)} \\ \hline 2C + 2H_2O \rightarrow CO_2 + \underline{\underline{CH_4}} & & \end{array}$$

(2) Gasification to hydrogen will be designed to use all types of coal; this flexibility is easier to achieve than in methanation. It will also allow, in the U.S., use of Eastern coal on-site, where water is abundant.

(3) The investment in *two* shift converters (one for coal → H_2 + CO , the other pre-existing in a Haber/reforming plant) is an unnecessary duplication, avoidable in constructing new manufacturing plants. For older plants "tuned" to use natural gas, it still saves more investment in equipment than it costs.

(4) In contrast to the hydrocarbon produced in more sophisticated methanation or liquifaction of coal, the hydrogen produced is cheaper for the same content of energy but not readily shipped or distributed as a general fuel. It will be used captively at the site of the Haber plant.

Prospects: A few decades should suffice for perfecting *and* deploying the technology on a wide scale. The immediate shortage of natural gas in the U.S. will supply much incentive in this nation. Energy-efficiency (hence dollar costs as well) will probably nearly equal that in reforming of natural gas. Some environmental problems will arise because coal carries more contaminants than natural gas. Worldwide, coal will supplant natural gas for the Haber process (and general use, perhaps) after these few decades. Coal-rich countries, particularly Russia and the U.S., will increasingly monopolize the manufacture of ammonia and nitrogenous fertilizers. Monopolization will be less drastic if nuclear-driven thermochemical generation of hydrogen (below, C) overcomes its obstacles of technological research (greater than here) and of public antipathy to nuclear power.

C. Thermochemical Generation of Hydrogen from Water

Nuclear reactors produce high-temperature heat, which — if usable efficiently — could replace fossil fuels for making hydrogen. While total energy resources might not be extended (nuclear energy is a limited resource as are fossil fuels, and shows much the same spectrum of end uses), the end use of nuclear power is made more flexible at least. Thus when convenient fossil fuels run out, nuclear power could substitute at the same or lower dollar cost, if it can be used to generate H_2 efficiently. The sequential conversion of energy as nuclear → electrical → chemical (H_2) has been shown inefficient in Sec. II.B, principally due to the first step. Direct use of nuclear energy as heat to decompose water is desired.

Many proposals for a workable thermochemical cycle have been made.[75a,76] A cycle is a sequence of reactions, one or more driven by heat, which effects the net decomposition $H_2O \rightarrow H_2 + \frac{1}{2} O_2$ while restoring all other reactants (it is thus regardable as catalytic). Molar conversion of water must be quantitative (without side reactions). Thermodynamic efficiency might be 50% in practice.[76] Heat sources at various temperatures are required, with the highest-temperature step sometimes being as low as 630°C. No cycle has proved practical on a large scale. Indeed, most proposals suffer from side reactions, or slowness of key reactions at low temperatures, or need for vast quantities of catalytic materials. Laboratory tests on several cycles have succeeded, but engineering a large-scale plant is proving difficult. Thus costing is purely speculative. The technology is likely to be perfected within the next decade, especially given the intensive efforts in Europe, and selective efforts in the U.S.

Heat from a nuclear reactor could be used at 50% efficiency to generate hydrogen directly *vs* hydrogen generated with 24% efficiency via electrolysis (Sec. II.B; 31.5% x 77%). This hydrogen is best used in chemical synthesis, at its full thermodynamic potential, rather than as fuel at 35% conversion.

Therefore, thermochemical generation is a limited strategy in the *total* energy budget. As noted in Sec. II.B, the net efficiency of synthesizing ammonia may be 38%, compared to 54% from fossil fuel. The cost-effectiveness of the overall process may also be reasonably favorable, if one speculates that the thermochemical apparatus is no more costly than electrical generation apparatus of equivalent capacity for a nuclear power plant. (Present estimates[76] for the best cycle are much worse.)

Prospects: A commercial cycle will be perfected in about a decade, given present or increased levels of research. For the few cycles likely to succeed, it is imperative to project the availability of materials for the next 50 years or so; some processes have hundreds of kilograms of cyclic reactants resident for each kilogram of water decomposed per cycle. Potential for pollution must be assessed, because some cycles employ volatile iodine or mercury which are threatening even at minor fractional losses. Technological problems and public antipathy to nuclear power in general will limit this option to a fraction of its potential.

D. A Short Note on More-Radical, Renewable Sources of Energy for Generating Hydrogen

Radical alternatives involving large-scale solar generation of electricity and fuel have received a measure of attention, particularly in the popular press. The three technologies are (1) windmills, indirectly tapping the global solar heating which drives atmospheric motion; (2) solar electric plants, using silicon photovoltaic cells or steam turbines; and (3) "energy farming" of crops in addition to food crops. The latter two tap solar energy in its most dilute form and require construction or planting over vast areas. Windmills need less area to tap an equivalent fraction of available energy. All three technologies are being designed to deliver electricity. Producing storable fuels -- feedstock for the Haber process particularly -- requires an extra, lossy step of electrolyzing water to hydrogen. An exception is solar thermal power, diverted from driving a steam turbine to running a thermochemical hydrogen generator directly. I estimate below from many partial references the energy deliverable by each method, as a fraction of total intensity of insolation on the land. Only output energies are quoted; the energetic cost of constructing the windmills or turbines or the like reduces the net energy delivered, by a large fraction for the first two technologies.

Wind

$$\text{Solar} \xrightarrow{2\%} \text{wind} \xrightarrow[10\%\ \text{max.avg.}]{\text{capture}} \boxed{\text{electric } 0.2\%} \xrightarrow[77\%]{\text{electrolysis}} \boxed{H_2 \ \ 0.15\%}$$

Energy crops

$$\begin{tikzcd}
\text{Solar} \arrow[r, "0.3\%", "\text{max. avg.}"'] & \text{biomass} \arrow[r, "\text{fermentation}", "75\%"'] & \text{chemical} \arrow[r, "\text{reforming}", "80\%"'] \arrow[dr, "\text{gas turbine}", "35\%"'] & \boxed{H_2 \ \ 0.18\%} \\
 & & & \boxed{\text{electric } 0.08\%}
\end{tikzcd}$$

Solar electric plants

$$\begin{tikzcd}
\underbrace{\text{Solar}}_{\text{at surface of earth}} \arrow[r, "10\%\ \text{avg.}"'] \arrow[drr, "\text{thermochemistry}", "30\%\ \text{duty x } 50\%\ \text{conversion}"'] & \boxed{\text{electric } 10\%} \arrow[r, "\text{electrolysis}", "77\%"'] & \boxed{H_2 \ \ 7.7\%} \\
 & & \boxed{H_2 \ \ 15\%}
\end{tikzcd}$$

Note that the most energy-intensive nation, the U.S., in 1975 used energy equivalent to 0.16% of the total insolation reaching its land area. Even if simple conservation measures reduce this figure to 0.10%, reliance on any of the above as principal power source requires that we develop perhaps 60% of total wind potential; or 60% of all land for energy crops; or 1% of all land for solar thermal/electric power. This implies great expenditures of material, energy, and capital for fabrication. For energy crops, it also implies using far more extra land than is actually arable, and land that is more valuable for producing food than energy; see below. None of these radical sources will be developed quickly, not even for limited use in providing hydrogen for the Haber process.

E. Generating Methane from Nonfossil Sources

Grown organic matter represents a renewable resource which may be fermented to methane with little or no additional energy. Methane is available directly[16-19] by fermenting crop residues or animal manure. It is at least practical for local use (if not central generation and distribution) as shown by 50 years' experience in France and India. Somewhat more efficient fermentation of cellulose to ethanol[16-20] indirectly makes hydrocarbon available for reforming, or for simple energy substitution which frees natural gas for use in the reforming process. I consider here only wastes from crops planted for food, not additional crops planted entirely for conversion to fuels. Roller *et al*[17] concluded that the ethanol produced from such additional crops is not competitive in the mass market. In particular, these crops compete poorly for use of land...even land that is marginal for growing either food or energy crops.

A third, abiological process is pyrolysis of urban wastes. It is energy-consuming in usual applications (but see Ref. 16) and only alleviates net costs of disposal.

It is not considered here that the methane generated would be shipped to a Haber plant, nor even shipped to a general market for methane off the farm. That is, I consider on-farm energy-substitution value, involving no cost of distribution and little cost of gathering waste to the generating facility. This is still more directly relevant to nitrogen nutrition of plants than strategies of pure energy-substitution not to be considered here, because removal of crop residues to the generator will deprive the land of the normal partial return of organic nitrogen via decay. (Restoration of nitrogenous waste to the field from the fermentor is likely to be marginally economical due to cost of hauling a fertilizer with no more than 4% nitrogen value.) It must be shown that (1) energy recovered (methane out minus expenditure in harvest) exceeds energy needed to make additional fertilizer to replace the organic residue, and (2) the dollar value of generated methane exceeds costs of harvesting, extra fertilizing, and amortization of the fermentor. Note that the energy in crop residue is not recovered in natural decay, so external recovery is a gain.

Heichel[14] has estimated that the energy expended to distribute animal manure at 33 metric tons/hectare (15 tons/acre) within a 5-km radius costs the equivalent of 280 liters of gasoline/ha (30 gal/acre). I shall use this same estimate for gathering crop residues, namely, 323 kJ/kg wet or 900 kJ/kg dry. One kg of dry waste yields 265-375 liters (at 16°C) of methane (converted to metric units from values in Ref. 75b), or $10^4 - 1.5 \times 10^4$ kJ. The amount of nitrogen removed is about 0.02 kg per dry kg, of which about 0.016 kg N normally would have been reutilized by the next crop. Fixed nitrogen costs 9.7×10^4 kJ/kg to replace by the reforming/Haber process. Thus (methanic energy out) - (gathering cost) - (energy to replace nitrogenous content) for 1kg of dry waste is (12450 - 920 - 1550)kJ ≃ +10000 kJ, a worthwhile gain. Methane produced is diluted with CO_2 but still usable even unpurified for cooking, e.g.

Several authors[16,20] discuss the economics of general recovery of energy in wastes, which economics is still debatable. Because natural gas currently costs about $\$1.70/10^6$ kJ ($\$1.80/10^6$Btu) delivered, the costs of collecting, fermenting, and replacing fertilizer should not exceed $1.70 for the net weight that provides a net gain of 10^6kJ, namely 280 kg wet; that is, they should not exceed about $6.10/metric ton. Transportation on the farm may be feasible, even a large one,[19] though probably not transportation to a large central plant.[77] Boardman and Larkum[16] quote a net figure of $\$0.95/10^6$ kJ for the cost of methane as delivered.

It remains to assess the effect of harvesting residues upon the quality of the land. Nitrogenous compounds removed can be replaced with fertilizer, but sufficient organic matter must remain to condition the soil. Because harvesting only above-ground portions is envisioned, the root material should suffice for most soils.

Prospects are quite good, considering that the technology of fermentation is already in use, though it requires some perfection of adaptation. Before most farms (in the U.S) adopt this strategy, (1) it must be proven economical in this country; and (2) potential manufacturers must assess acceptability to the farmer of the additional field chores and items of maintenance.

IV. APPROACH THREE. OPTIMIZE THE USE OF NITROGEN-SOURCES BY A GIVEN PLANT

Both natural sources of nitrogen and synthetic fertilizers may suffer ultimate losses via denitrification, leaching and runoff, and harvesting of crops without return of wastes. Both may also accumulate in excess which needlessly ties up "nitrogenous capital" usable elsewhere. Lastly, the original ammoniacal form may lose thermodynamic potential by conversion to nitrate, causing plants to expend slightly more energy (10% of total yield) in assimilation and to yield less crop.

A. Upgrading Management on the Average Farm

Leaching and runoff of nitrogenous compounds are problems generally attributable to poor management of a farm, hence remediable with present technology and concepts of management. Motivation for most current work on-and off-farm on reducing leaching and runoff is the prevention of water pollution by low-level losses, not the appreciable loss of soil nitrogen. Loose soil structures in some geographic areas will always be problematic, but only the worst cases of land that must be cultivated should be left unremedied—a small fraction. Occasionally, deep-rooted crops such as alfalfa could be used to assimilate nitrogen that leaches beyond normal root zones.[45] The favored ammoniacal form of fertilizer in use today in developed countries suffers losses by direct evaporation[39] when faulty injection equipment is used or if it is applied in irrigating water; these problems are of moderate extent.

Denitrification can be a significant loss when soil is alkaline and anaerobic—very wet and compact. Annually, episodes of anaerobism are routine in most areas of the U.S. or the world, due to episodes of heavy rains, for example. Deep tilling and even ordinary seeding counter the trend to anaerobism but are not remedial in mid-crop; furthermore, tilling is rather energy-intensive, consuming perhaps half of the gasoline for tractors (about equal to the energy-equivalent of fertilizers).[78] Tilling may be progressively minimized[13-15] for the partial saving of energy (30% of the energy expended in tilling now, according to Heichel[14]), lowered rates of erosion and leaching, and actually increased yield[13]...apparently anaerobism is not aggravated. Seeding alone does not aerate the future root zone. Nonetheless, average denitrification on the U.S. agricultural land is probably held to about 2% of soil reserves (but 70% of annual fertilizer input) with present practices. (Natural ecosystems probably fare as well.)

Both denitrification and leaching can be highly suppressed by preventing the initial nitrification of ammonia to nitrate, by applying the compound N-Serve.® Yields of all types of crops rise[2d,47-49] quite uniformly by 10-15%. I attribute about half the rise to lessened metabolic costs of assimilating ammonia instead of nitrate (*cf* App. B). The remainder of the gain is lessened leaching and denitrification of excesses of nitrate formed so commonly in intensive agriculture[47] (excess is that portion unused in the growing season). Use of N-Serve® is increasing, perhaps more slowly than merited because reducing use of fertilizer *appears* to be risking yield.

Total fertilization often is excessive in intensive agriculture, when farmers strive for the best total yield and not best yield per unit of resources used (App. A, Sec. II). Excesses of nitrate are partly remedied biannually in high-management farming by use of low-nitrogen, highphosphorous-sulfur-potassium fertilizers. The fate of excess nitrogen is not always accelerated loss, moreover. It may go into increased organic matter, where it simply remains tied up, ammonifying to assimilable form at only 3-4% per year. Still, it does represent at least a tying-up of nitrogen usable elsewhere; it should be discouraged economically by lessening the partly-artificial competition in markêts (governmental action on subsidies) and should be remedied by developing field tests for its presence.

Prospects: A comprehensive strategy of new management then consists of tilling less, suppressing nitrification, and applying ammoniacal fertilizer only to sufficiency and not excess. Field-testing for sufficiency of nitrogen in soil is improving but still is not accurate enough;[51,52] it deserves considerably more research effort now that fertilizers are less available. Low-till and no-till agriculture is being proven in field tests currently. Use of N-Serve® is proving economically feasible in general use and may become even more attractive when tests of nitrogen-sufficiency improve. Tests should be made to evaluate separately the gains in yield due to lower losses of nitrate and the gains due to lower metabolic costs of assimilating NH_3.

B. Reclaiming Sewage

The 20$^+$% of newly-incorporated nitrogen represented by harvestable parts[37] of a crop is almost never returned to the same soil. Rather, it ends up as animal and human waste, the latter being very localized in human settlements, be they cities or villages. Wastes in urbanized countries generally end up as sewage. Sewage can be processed to a pathogen-free, unobjectionably-odored fertilizer which is reasonably balanced in nutrient elements. The fraction of waste so returned to the soil is very small presently, limited by costs of transportation to a small radius around the cities. Thirty kilometers may be reasonable, more if costs of synthetic fertilizers rise dramatically.[79] The fraction of agricultural land so covered is very small. Compare Heichel's[14] estimates on animal manure in Sec. III.D. In contrast to material with a high energy value such as crop residue, sewage is valued only for its 2.5-6.5% content of nitrogen.[79] (The remaining 90$^+$% has much less value, as a soil conditioner.) A minor incentive to transport treated sewage somewhat further than is justified by its value as fertilizer is reducing its negative value as a disposal problem. When disposal is the principal concern, the rate of application may be chosen so high as to exceed usability by plants. Excess nitrogen exposed in surface application as volatile ammonia (30-50% of total N) will evaporate and be lost.

Prospects: Urbanization, as explained above, restricts this strategy to a few-percent return of the nitrogenous wastes, equal to 1% or less return of total needs of crops, at least in developed countries. Urbanization may decrease in the next decades but not enough. Reclamation of digested sewage will remain a very minor strategy in nitrogen-nutrition of crops. It will be regarded as a strategy to solve the unrelated problem of waste disposal and its development will be guided by this consideration almost exclusively.

V. APPROACH FOUR. OPEN NEW ROUTES FOR BIOLOGICAL FIXATION OF NITROGEN

On the world's land which is planted to harvested crops (not forage land), biological fixation is estimated to supply just over half of all fixed nitrogen (App. A, Sec. I.A) or 44 million metric tons. This fraction is shrinking as synthetic fixation into ammonia rises and as the absolute quantity of biological fixation is increasingly suppressed by the application of nitrogenous fertilizers. In the very long run of centuries, biological fixation will have to increase both its fractional and absolute contributions; total fixation must rise to meet demand for food, while synthesis of fertilizer will be curtailed by a drop in supply of energy.

Of the two types of biological fixers, symbionts outdo free-living fixers on harvested land. Symbiotic bacteria in legumes fix about 35 Tg per year, while blue-green algae and bacteria — the free-living fixers — contribute about 9 Tg.[30] (On forage land, the free-living microbes contribute most of the estimated 45 Tg. Forage contributes indirectly only a small fraction to human food, however.) More relevantly to strategies of management, the ecological niche for free-living blue-green algae and bacteria has little promise for expansion: (1) on most nontropical soils which are not wet, fixation is quite low naturally;[21] and (2) Watanabe[80] has experimentally enhanced algal populations in semi-tropical rice paddies but increases in crop yields were not persistent. This inflexibility may be because algae require for good growth[21b,81] both air and light, available only in a thin 1-cm layer of soil. Only a few blue-green algae (all normally photosynthetic) can fix nitrogen heterotrophically (*vs* photosynthetically) when light is not available, and most of these do so aerobically. In all nonphotosynthetic or anaerobic conditions the rate is quite low.[21b] Overall, the free-living microbes have an efficiency about 10% that of root symbioses, in consumption of organic energy (carbohydrate, self-fixed or from decay) per unit of nitrogen fixed.[32]

The range of plants of any phylum which have symbioses with fixing algae or bacteria is rather limited,[11,28,21d] and among crop plants the range is restricted to legumes with their characteristic root nodules harboring species of *Rhizobium*. On most arable land, existing legumes have limited promise of increased use. (1) As food crops their contribution to the human diet is limited by (a) need for foods providing a higher percentage of calories relative to protein, (b) established tastes, and (c) their low yield per hectare relative to other crops. (Even given synthetic fertilizers, grain legumes such as beans or peas, do not yield well.[40b]) (2) As animal forage such as alfalfa, their above-ground portions (a) contribute only about 10% of their food value to humans,[14] compared to 40% (the harvested portion)[37] if an alternate legume is eaten directly; (b) can be replaced by uncultivated forage on open rangeland *if* present trends to local overgrazing are rigorously checked. (3) As cover during fallow periods that cannot be exploited for crops, legumes can supply organic nitrogen for the next crop,[11b] *but* this technique is useful and practical only in quite limited geographical areas. Lastly, legumes fix only an average of 25-30% of their annual needs[40a] by themselves without fertilization, and less even on an absolute basis when fertilized.

Therefore, many researchers are seeking to "create new legumes" out of major crops, particularly cereal grains comprising the major fraction of all food crops. The search has begun for modifications in crops and/or nitrogen-fixing bacteria that will allow new root symbioses. Looser associations of blue-green algae or bacteria with leaves of plants are also promising; these occur naturally[21d] and may be easier to extend to new partners. A more radical, and permanent, strategy than effecting new symbioses is to transfer into the crop plant those genes coding for the nitrogenase enzyme and related structural needs.

In order to raise the fraction of needed nitrogen which plants can fix for themselves, other researchers seek to derepress the (*Nif*) genes for nitrogen-fixation, or to suppress the energetic drain due to photorespiration. Photorespiration is a wasteful consumption of cH and oxygen, in excess of normal respiration needed for growth and repair, and perhaps even representing an "evolutionary mistake" avoided in very few plants. Successful suppression would raise yields in general and may disproportionately[11c4a,54] aid the fixation of nitrogen.

Lastly, algae are being tested as unconventional crops that can fix their own nitrogen and perhaps utilize some wastes from power plants at the same time. I examine each of these approaches in turn.

A. Root Symbionts

Nitrogen-fixing bacteria enter the root tissue of select plant species, undergoing quite a change in form to "bacteroids." They tap the plant's carbohydrate (cH) supply (about 2400 kJ worth of cH per mole of NH_3 made, or 3.8 times as much energy as the Haber process uses - see App. B, Sec. II.B), respire aerobically, and transport amino acids or direct precursors[28a,29] into the plant tissue. This aerobism is remarkable, because the nitrogenase enzyme is very sensitive to inactivation by oxygen. The roots, with their low internal concentration of oxygen, are an ideal site for protection from oxygen. At the same time, the iron-heme protein leghemoglobin made by bacteroids appears to assist the aerobic respiration.[11,82]

The great majority of fixed nitrogen is given to the plant,[61a] yet some control is exercised in that high levels of glutamate and ammonia decrease the rate of initial synthesis of enzyme.[11d,28b,83] Thus in practice about 30% of the total needs of the host plant are supplied. Were control lacking, the bacteria might overspend their energy relative to that needed for growth and maintenance. The plant might also suffer from excess synthesis of protein, leading to structural weakness and inhibited fruiting.[2a,6a,55,56a,84a] (Most of the fixed nitrogen *is* supplied at fruiting time,[40a,54] but a corresponding drop in uptake of soil nitrate avoids inhibiting the process of fruiting.)

These symbiotic associations are quite specific and limited in nature. Even bacteria-host pairs proven capable of symbioses often show low rates of success. Inoculation of pea seedlings with massive doses of natural *Rhizobium* is only 5% successful,[85] and other inocula are often not persistent.[86] Competition with native soil microflora apparently underlies many poor results. Consider also that symbiosis is divided by a fine line from harmful pathogenic infection, depending on the balance of benefits to both partners. Successful plant species, leguminous or not, tend to exclude almost every bacterium to protect themselves.[87] These observations temper the hope of finding new crop symbionts which are stable in varied soil environments. The task of finding symbionts for each crop species is expensive and time-consuming, even neglecting the complication of finding a symbiont for each type of soil and weather. Only one new symbiosis has been successful in laboratory culture, and only with root cells, not with a whole plant.[88] The chemical "signals" exchanged by plant and host are being deciphered right now[11e]... signals that turn on rapid fixation by normal symbionts, and signals that determine the extreme specificity of symbiotic associations (lectin proteins, perhaps). (Despite great specificity of the pair, the bacterium carries all the genes needed for actual fixation and needs no products coded by the plant's genes.[11e]) The amount of research necessary is very great, to be sure.

Prospects: Considering the magnitude of the task as outlined, I subjectively estimate that 50 years of intensive research will pass before successful symbionts are found for most crops. Concentration on crops that supply most food calories in the average human diet worldwide is definitely advised. As noted in App. B, the work of fixation will burden the metabolism of a crop just as in legumes today. Yield will decrease perhaps 6%, such that even successful symbionts would be no more than competitive economically with synthetic fertilizers, for as long a time as costs of the Haber process rise in very crude proportion to net costs of food. Besides similar direct costs in yield, synthetic fertilization and symbiotic inoculation probably would have similar labor costs for field-application.

Much research in progress is very basic. (1) Studies on the nitrogenase enzymatic complex include its structure, chemical intermediates in fixing action, requirements in energy and chemical cofactors, means of indirectly utilizing oxidative energy carried by leghemoglobin, and model catalytic compounds. (2) Research on mechanisms controlling net rate of fixation covers the chemical species involved, and kinetic constants. (3) Signals between symbiotic partners allowing "infection", and further signals to initiate strong fixation, are being studied. Research of type (3) is most relevant to nitrogen-nutrition by new symbioses. Types (1) and (2) are more tangential to the aim of getting practical symbioses (after all, we know that the nitrogenase system does work) and these efforts should be supported rather separately from (3). Additional research of a more applied nature is also needed, on factors in the competition among soil microorganisms affecting survival of the bacterial symbiont. It will narrow the ultimate task of screening many "symbioses" to find the few that will work in the field.

B. Leaf "Symbionts"

Symbiotic or looser associations of bacteria and blue-green algae with leaves of vascular plants are not rare in the wet tropics.[21d,89] The fixing organisms are of many genera; surveys have not been sufficiently thorough[89a] to establish relative importances to the ecology. Few types of these organisms are found living free in the soil, for unknown reasons.[89b] They function as weak aerobes, crowding together in thick blooms perhaps to reduce oxygen concentration locally. Though some species might be capable of photosynthesis, they live off carbohydrates exuded by host leaves through the weakened waxy cuticle,[89c] weakened by the action of the microbes themselves. (Confusion of symbiosis with actual parasitism is possible without careful observation.) In turn, the microbes excrete quantities of fixed nitrogen. In one regenerating forest,[90] annual fixation appeared to be 70 kg/ha embodied in living matter and another 580 kg/ha in the soil! This total rate exceeds that of intensive synthetic fertilization, and vastly exceeds rates of fixation by free-living microbes in the soil. Excretion of fixed nitrogen is not a specific response to the "host," but a general property (of blue-green algae, at least[21e]) due to the simplicity of the organisms and consequent primitive control of metabolism.

Extension to major food crops is a very tenuous prospect at present. A very wet climate is necessary, and even then the microbes fluorish only in occasional flushes.[89d] Only one cultivated crop, cocoa, naturally has the "symbionts." In drier climates, microbial cultures sprayed on the leaves might function at a low level despite persistent dessication, thereby supplying a few percent of the host's needs for nitrogen. A. Watanabe (Seijo Univ., Tokyo) is reportedly experimenting along these lines. The hazard of inadvertently introducing a parasite rather than a symbiont is present, but at least the requirements for coexistence/symbiosis may be less stringent than those for root symbionts (but see Ref. 89e). It is not to be feared that microbial blooms partially shading the leaves from sunlight will decrease yield of photosynthesis. Plants growing in natural atmospheric concentrations of carbon dioxide are limited by the availability of CO_2 (coupled to the availability of water, because leaves open to entry of CO_2 are open to loss of water).[59b] Thus they are supersaturated with sunlight relative to CO_2, and adjust admirably to a decrease in available sunlight,[91] as by increasing their content of chlorophyll or growing more leaf area.

Prospects: Worldwide, agriculture is pursued mostly outside the tropics.[90] Successful "symbioses" for general agriculture may be found in one or two decades of intensive work, and may yield perhaps one-tenth the benefit that root symbionts provide (or 3% of needs). Due to the low level of benefits, the work will probably progress more slowly, over a span of 50 years.

C. Transfer of *Nif* Genes into Host

Nitrogen-fixing ability in the bacteria responsible for legumes' success is due to a few enzymes and some structural details. Were the (*Nif*) genes that code for these enzymes to be added to a crop plant, it and all its offspring might be able to fix their own nitrogen. For ordinary legumes, this would make unnecessary the inoculation of seeds with bacterial cultures, which is only moderately successful (Sec. A above). Fixation could be independent of soil conditions. Of even greater impact would be the transfer of genes to nonlegumes, enabling them for the first time to fix their own nitrogen. The procedure for transferring genes is likely to have less specific conditions than finding a separate symbiont for each species of plant.

Serious problems must be overcome: (1) Nitrogenase enzyme (N_2ase) which does the actual fixation is very sensitive to oxygen (Sec. A). In natural symbioses, the low level of soil oxygen, specialized cellular membranes, and leghemoglobin all act to keep concentrations of free oxygen low near the nitrogenase, yet high enough at respiratory centers which supply energy to nitrogenase as ATP molecules. In the cells of a vascular plant, the proper structures are unlikely to form spontaneously. They are also unlikely to be transferrable genetically as a simple set of genes...more likely as a complete structural plan. Indeed, there is an evolutionary argument[29a] proposing to explain why higher plants never evolved nitrogen-fixing ability despite millions of years' contact with able microbes: higher plants are too committed to aerobism and unable to make the radical, extensive changes in structure necessary to accomodate "pockets" of anaerobic fixation. (2) Even if genes are successfully incorporated, translation into protein structure may fail,[92] e.g., the protein may fold incorrectly in its new environment. (3) *Nif* genes are coupled in function but perhaps not in spatial location on the genome to other necessary genes — such as those for special membranes or for leghemoglobin. Locating all the genes to be transferred and placing them properly in the new genome may be very difficult. (4) Higher plants show great diversity or differentiation of cells into many types; even within leaves, for example, there are epidermal cells, vascular tissues, guard cells, etc. *Nif* genes should probably not be expressed in most types of cells. In leaf cells that evolve oxygen, N_2ase would be rapidly inactivated, and uncontrolled resynthesis could drain much energy from growth of the plant.[93] Controlling the differential expression of *Nif* genes is another order of difficulty above gene transfer. (5) There is a problem of public policy, namely, that genetic engineering is very hazardous, especially in the use of pathogenic bacteria for thorough testing of techniques. Although nitrogen-fixing bacteria are not pathogenic, experiments on pathogens are needed to perfect genetic transfers. A moratorium or severe set of restrictions on research is likely and advised even by many scientists.[94]

There are rays of hope. *Nif* genes have been transferred[95] to the common gut bacterium *E. coli* that is totally unrelated to fixing organisms. The genes operate, even if only under anaerobic conditions due to the lack in *E. coli* of structures protecting N_2ase from oxygen. (Anaerobic respiration to supply energy for fixation is not feasible for higher plants. Accumulating metabolites are toxic. Also, anaerobic respiration is only about 5% as efficient as aerobic, yielding two ATP molecules per hexose sugar consumed, compared to 38 yielded aerobically.) Another hopeful sign is that *Nif* genes have been transferred[96] from an anaerobic bacterium of the genus *Klebsiella* to the aerobic *Azotobacter vinelandii*. The latter normally fixes nitrogen, but a defective mutant was selected. The significance is that *Nif* genes can be expressed in good cooperation with genes for oxygen-protective structures coded elsewhere in the genome.

Prospects: Transfer of *Nif* genes which retains proper expression of these genes will likely take even longer to perfect than artificial symbiosis. I suggest 100 years, if ever. It is the superior strategy of all, but it will not be perfected in time to meet the crucial need for nitrogen-nutrition in the next 50 years. Research will continue, aimed at problems (1)-(5) above. It needs less advocacy by scientists to funding and policy agencies than other radical strategies, because it has strong ties to high-priority medical research.

D. Derepression of Nitrogen-Fixing Genes

In order to make symbionts to legumes (or to other species, if strategy A succeeds) provide more than the typical 30% of the nitrogen-needs of higher plants, one might hope to remove controls that limit rates of fixation. The primary control (Sec. A) is negative feedback of synthesized glutamate upon the synthesis of N_2ase enzyme. At predetermined concentrations of glutamate representing fixed product, the synthesis of nitrogenase decreases and finally ceases. Derepressed mutants of the anaerobic genus *Klebsiella*, but no such mutants of common leguminous symbionts,have been found. A chemical means of derepression, rather than a genetic one, may well be preferred anyway. Permanent derepression could overnourish the plant with nitrogen relative to carbohydrate, leading to devastating symptoms described in Sec. A. A chemical which alters the level of feedback could be withheld when fixed nitrogen became excessive. J. Gordon[97] has found a chemical, methionine sulfoxime, which performs such a task *in vitro*. Though impractical in the field, it is a first step.

Prospects: This strategy could help leguminous crops or any crops for which strategy A will find new symbionts. It will not help the majority, at least for many decades. Still, screening of chemicals to find a useful derepressant is easier than selective breeding of mutant symbionts that are derepressed. The strategy may become practical in a few decades. Field testing of nitrogen sufficiency in crops must be perfected in order to use it.

E. Suppression of Photorespiration

Plants ordinarily respire at all times, consuming carbohydrate (CH) and oxygen in an overall (but not stepwise) reversal of photosynthesis. Respiration liberates energy for tasks of growth and repair. Dark respiration proceeds in several stages — glycolysis, citric-acid cycling, and oxidative phosphorylation — with a few modified pathways in parallel.[59c] It is aerobic and the most efficient form of respiration. It is essentially independent of photosynthesis, being regulated by temperature and other gross factors. Photorespiration (PR),[56b,98,99,100a] on the other hand, is an additional consumption of cH and O_2 which is directly related to the level of illumination. Its irreversible chain of reactions begins in the chloroplasts, then proceeds to the general cytosol and the mitochondria where the steps of dark respiration occur. Like dark respiration, PR yields CO_2 and water ultimately, through an intermediate stage of glyoxalate. However, it yields little or no useful energy. It is functionally described[98a] as either: (1) a route to simply dump excess energy which the plant is unable to use fast enough (excess reducing agents generated in photosynthesis might threaten to damage chlorophyll), or (2) an evolutionary mistake in which the enzyme ribulose diphosphate carboxylase functions not only to assimilate CO_2 into sugars, but also to add oxygen destructively to these same sugars. These viewpoints may not be mutually exclusive, or inclusive either.

Photosynthesis itself drops when plants must conserve water, reducing their water transpiration by closing leaf openings or stomata. This closure cuts off transport of air into the leaf as well as out of it. Thus it causes a deficit of CO_2 needed for photosynthesis, but this deficit is less serious than a deficit of water. The air trapped inside the leaf at closure is depleted of its CO_2 down to a lower limit depending upon the type of plant. At the lower limit, PR balances photosynthesis (PS).

Rates of PR at a given illimination and water supply fall into two broad ranges. Low rates, to near-negligibility, are common in certain tropical grasses, including corn, and some desert plants. Clearly a low rate is an advantage, since water deficit is common in bright sun and dry weather; low rates of PR at least keep the net gain (PS)-(PR) high. These plants generally share another feature, the newly-discovered "C_4 path" of fixing carbon dioxide into carbohydrate. The C_4 path involves gross structural differences[100b] and an extra enzyme of higher affinity for CO_2 than the primary fixer in the normal C_3 path. This enzyme also avoids the "mistake" of accepting O_2 instead of CO_2, which initiates PR in C_3 plants. PS can proceed to lower concentrations of CO_2 in the inner air-spaces of the leaf, typically 5 ppm *vs* 40 ppm for C_3 plants. Under the same conditions of weather and soil (except *cold* weather), C_4 plants typically outproduce C_3 plants in biomass by a factor of two to four.

Were the C_4 path capable of being bred into other major (C_3) crops than corn (C_4), it could raise yields dramatically. Nitrogen fixation by symbionts could be multiplied even more than total yield,[11c,40a,54] because circulating carbohydrate (cH) would rise more than crude yield of photosynthesis. That is, local use of cH by the shoot would saturate, leaving an excess above threshold available to circulate to roots. At the roots, increased cH leads to increased activity of N_2ase, more nodules, and longer activity of nodules.[40a,54] Genetic transfer of the C_4 enzyme alone is likely to be less complicated than transfer of *Nif* genes but is less seriously pursued. The need for structural changes to accompany the enzyme is unassessed, whereas in *Nif* transfer they are known to be needed. A simpler task appears to be simply repressing PR in the C_3 plants, allowing PS to remain limited by CO_2-deficit as before. (1) Levels of photorespiration within a given species seem to be under genetic control. Classical selection programs may succeed, though initial results have been somewhat disappointing: the trait of low PR does not stabilize[101] so that it "breeds true." (2) Externally-applied chemicals[102,103] show promise of suppressing PR. Full-scale field tests remain to be done, on extent of suppression of PR, on long-term effects on the plant's viability and its food value, on economic feasibility, and on generality of use (all C_3 species, or at least broad families?).

<u>Prospects</u>: (1) Screening of chemicals for suppression of photorespiration and the other necessary characteristics noted above can begin immediately. The recent successes in suppressing PR in individual plants give hope that success lies a decade or two away. (2) Breeding programs for low rates of PR may be successful later. Extension of existing breeding programs for other traits is not completely straightforward, as initial results[101] have shown. Simply increased yield indicates low PR, but stabilization of the trait apparently requires attention to subtler details. (3) Basic research needed to support (1) and (2) includes: (a) uncovering the genetic basis of photorespiratory rates (how many genes, for a start) and (b) assessing the function or dysfunction represented by PR; if PR *does* prevent damage to chlorophyll from excess reductant generated in PS, can we suppress PR continuously and expect to avoid the damage?

F. Algal Farming

Although all plants can utilize light at high efficiences[104,105] over short periods, many algae can do so over many generation times.[105] They are, after a fashion, edible by humans[106] and more so if used as a food additive or as extracts of their protein, carbohydrate, or fat. Algae may also serve as feed for livestock. Their requirements are rather simple, inorganic nutrients in solution,[107] such that growing tanks could be located to utilize totally unarable land. This most unconventional crop then does not have to compete with ordinary crops for land use especially. Ordinary crops win over other unconventional crops such as in "energy farming".[17] Their balance of inorganic nutrients, particularly iron and sulfur, can condition them to yield predominantly protein, fat, or carbohydrate as desired.[105b,107a,108] Liquid solutions in which they grow are easier to handle in many ways than soils and other solids. Algae, as all plants, increase their yield almost in proportion to the concentration of carbon dioxide[99a,107] (for somewhat different reasons[109]). This concentration might be increased by applying otherwise-wasted stack gases from a fossil-fueled power plant[91,110] to the growing tanks. This is much easier[112] than applying stack gases to large areas of farmed soil.[111] The waste heat also aids growth. Barring the use of stack gases, natural fresh-water lakes may be "farmed."[113] Finally, of greatest relevance is that algae might fix their own nitrogen, or the major fraction in contrast to other crops. Only blue-green algae can fix nitrogen, so that if green algae are desired they must be grown in mixed culture with blue-greens, absorbing their excreted ammonia.[21e]

Unfavorable aspects of mass algal culture are also many, such that no venture has proved commercially successful to date. The Carnegie Institute of Washington ran extensive tests around 1950. The foremost problem is the high cost of environmental control: the growing tanks, monitoring of nutrients, power to stir solutions, aseptic measures to exclude pathogens. The equivalent energy[115] expended per calorie of food derived lies nearer that for leafy vegetables[14] in greenhouses (50:1) than that for open-field farming (as low as 1:3). Dollar costs are uncompetitively high, per unit of food value. A second major obstacle is that growth in strong sunlight is far from efficient in using light. Algal photosynthesis saturates at only about 4300 $\ell m/m^2$ of illumination[107] (or 22000 max., with CO_2 enrichment[105a]) though algae may get 86,000 $\ell m/m^2$ in direct sunlight. The excess is wasted, even if CO_2 is superabundant. Outdoor-tank growth is thus reduced to an efficiency of using light near 2-3% even with added CO_2, the same as for the best land crops such as sugar cane with added CO_2. The greater yield does not cover the costs incurred. Fortunately, yield has proved to be sustained, and used solutions do not seem to contain any subtle growth inhibitors[107] that would be hard to remove. For closed-tank cultures, solutions must be reused to conserve water in unarable lands (even though the 100 volumes of water used per volume of algae is exceeded in normal agriculture[59d] using perhaps 1000 volumes of water per volume of crop). At high production levels required for economy, water transport would be limiting without reuse. Filtration of water needs to be perfected particularly if stack gases are used for nutrition. These gases carry particulates that cloud the water, and perhaps light hydrocarbons that seem to be toxic to algae at quite low concentrations. (In contrast, some metallic and semi-metallic trace elements such as copper or molybdenum are nutritious to algae: others may be toxic, such as mercury. Emission levels are being measured;[116,117] toxic levels need to be established. Cheap filters may be available.[118] Major "contaminants", the nitrogen oxides NO_x and sulfur dioxide SO_2 are also potentially nutritious. SO_2 might supply most of the required sulfur, if it is oxidizable to sulfate rapidly enough.) Lastly, for use as a human food algae must be considerably improved in palatability. Unusual textures and flavors are often unacceptable[119] in replacing familiar ones in diets of less-developed countries, though care in presentation may help much.[120]

Prospects: Algae will not be a major crop anywhere because suitable sites, particularly the economically-attractive sites at power plants, are limited. Engineering research to reduce the high cost of environmental control will be done only following successful demonstration of continuous culture in high yield in open sunlight. One might assume that 2-3 decades will elapse. Research is needed over the same period on needs for and toxicity of trace elements, optimally-suited strains of algae (with higher saturating value of illumination, higher optimal temperature[107]), improved palatability to humans, and value of algae as cattle fodder. Coordinated research and development is yet lacking, and may frustrate the strategy entirely.

VI. APPROACH FIVE. UTILIZE CROPS FOR FOOD MORE EFFECTIVELY

There are at least three ways in which a given amount of assimilated nitrogen yields more or better food. (1) One plants available land with available species of crops that give the best return = greatest harvestable fraction by weight, or best protein per unit weight. One might expand the criterion to best return in food calories per unit of "cultural energy" -- tilling, fertilizer, etc. -- since energy and availability of synthetic fertilizer are closely tied (Sec. III.D). (2) One breeds new plants for the same goal. Rice strains bred for the "Green Revolution" are not relevant here. They simply yield more heavily per acre but use considerable amounts of nitrogenous fertilizer; that is, they conserve *land*, not energy. (3) One uses parts of the crop not normally considered edible, such as protein from leaves which are mostly indigestible to humans.

A. Selecting Crops That Give Best Return

This entails a progressive shift from "poor" to "good" crops in a national market, hence in relative availability of different foods to the consumer — promoting peanuts and restricting greenhouse vegetables, for example. One obvious prospect often stressed in the past is replacing meat by grains in developed countries. This bypasses the step of grain-to-meat conversion interposed between field and consumer, a step operating at only 5-18% efficiency in energy.[14,121] The gain in food energy available to humans per unit of energy expended in agriculture would not be as high as the 5.5-20 times suggested by the efficiency. Much of the crop fed to cattle is unusable by humans, who cannot digest cellulose. Also, livestock forage on unarable land. The net gain might be a factor of two for those food calories so replaced. Within the class of crops consumed directly by humans there are still great differences. Fresh vegetables are up to 50 times[14] as intensive of energy as grains. Because vegetables are not grown for caloric value but for other nutritional values, replacement can be only partial, and net gain may be a factor of two for these calories. Given that one wants good vegetable protein, one still must choose between, say, legumes and peanuts. Legumes are quite superior in using energy.[14]

Prospects: Dietary flexibility is a prerequisite for this strategy, limiting it essentially to developed countries. As a whole, this strategy is purely one of policy: who shall plant what crops, who shall market what foods. The only technological and scientific input is pointing out superior foods, which requires little effort other than keeping informed about new agricultural practices. Differences in prices to consumers, insofar as they reflect costs of fertilizer and energy, will help to implement the strategy, but only minimally: (1) developed countries will return considerable affluence and will exercise much of it on choice of food; and (2) prices to consumers also reflect widely-disparate levels of governmental subsidies to farmers. Revision of subsidies is necessary, but the consideration of saving nitrogenous fertilizer and energy will not be a major one until too late, perhaps. Prospects for this strategy being used in timely fashion are virtually absent.

B. Breeding Crops That Give the Best Return

Very little agricultural research has this goal at present; instead it aims at maximum yield per acre, disease-resistances, or other factors only peripheral to nitrogen- and energy-intensiveness. Strategy A above must be operating before any effort can be expected here. Therefore, prospects are virtually absent.

C. Processing Inedible Parts of Crops to Edibility

Millenia of trial and error have revealed the directly edible portions of various plants, and some portions which are edible after simple treatment, such as cassava root soaked and heated to remove poisonous hydrogen cyanide. High technology has yet to add to the list of palatable, widely-accepted, edible portions. Under development, however, is leaf protein[22] extracted from grains, cover crops, fodders, seed crops, etc. Uses by humans and livestock are both envisioned. A small group of investigators have tested palatability and nutritional value, with encouraging results. Extracting the protein cheaply is the major problem; much mechanical energy is used to break down the fibrous leaves.

Prospects: A rough doubling of available protein might be envisioned. Much leafy waste, however, is contaminated by alkaloids, tannins, etc., which may require inordinate expense to remove. Toxicities are often known, but impalatabilities are often unknown, so that testing is required. Mechanical-extraction problems will likely be overcome in a decade of effort once interest is stimulated in another decade. Adoption in developed countries (even for export) should lag by one or two decades behind that in less-developed countries. It is precisely in the intensive agriculture of the former, however, that the greatest absolute savings of nitrogenous fertilizer and of energy are possible.

NOTE ADDED IN PROOF

Transport losses, App. A, p. 15: *volatilization* of nitrogenous compounds, principally NH_3 , seems to be an important global transport of fixed nitrogen. It merits more attention than I implied by calling it a "miscellaneous loss." Burns and Hardy[30] have assessed it, based on work by many authors. Ammonia volatilizes from soil (a minor amount from the sea) and returns in rain, partly oxidized to nitrate. The local rate of volatilization averages only 10 kg/ha annually, or less than 10% of fertilizers where these are applied, but the global sum is 170 Tg/yr, equal in size to new biological fixation. The return in rain does not balance volatilization locally. The land loses perhaps 50 Tg to the sea, and the nitrogen-rich areas of land lose to the poor ones.

Airborne dust containing organic nitrogen (as humus) may transport 75 Tg/yr.[30] Net redistribution of fixed nitrogen from land to sea and rich to poor areas surely results.

Miscellaneous losses, App. A, p. 16: Purely *chemical denitrification*[30,122] may occur by reactions of nitrite with *organic* nitrogen also; the reactions are poorly understood at present. Innocuous N_2 is formed, it seems.

In contrast, McElroy[123] and Crutzen[124] warn of aerial N_2O pollution from *biological* denitrification, enhanced because intensive agriculture raises the levels of nitrite and ammonia in the soil. Quantitative estimates are still uncertain. I point out that agricultural land as a whole supports an annual gross production of biomass per area (denitrification per area, also?) equalling that for wild land. Intensively cultivated land supports a higher net production per area than the average.

General controls (over assimilation of nitrogen), App. B, p. 24: With modern breeds of crops, the hazard of excess nitrogen causing excessive vegetative growth and poor reproduction has been increased. These crops have been selected for gigantism of fruiting parts. To favor this growth of fruits, one must use *sub*-normal amounts of nitrogen.[125] Best yield of fruiting parts requires partly stunted growth, hence careful management. The utility of, and need for, fertilizers is reduced with new breeds.

Cost of Reducing Nitrate to Ammonia, App. B, pp. 25-26: Penning de Vries *et al*[126] have calculated theoretical respiratory losses in synthesizing final plant material from the raw carbohydrate provided by photosynthesis. Their results are substantiated by experiments rather well. With NH_3 as a nitrogen source, the work of synthesis consumes 25% of the initial carbohydrate. With NO_3^-, the consumption is 35%. Primary dry-yield of the plant is therefore decreased 12% by having to use nitrate. Because work of maintenance must be performed in either case and causes another drop in yield (the same for both nitrogenous forms), the fractional loss in final dry yield is diluted to about 6%. This agrees well with my estimates under the titles "internal economy" and "field tests."

Prospects for the Haber Process (whole energy expenditure in agriculture), App. C, p. 35: A corporate study[127] claims to be the most definitive study to date on energy used for agriculture. Their estimate for use on-farm is 2.5%, exclusive of transportation of inputs to the farm. This supports the 2.6% I have quoted. Their estimate for total use, exclusive of preparation (cooking), is 11%, higher than the 7.8% I quoted.

Leaf "Symbionts," App. C, p. 51: The proposed restriction of natural associative symbioses to tropical areas may be untrue. A few temperate crops[128] and especially temperate woods[129] may benefit significantly from these loosely symbiotic fixers.

Suppression of Photorespiration, App. C, pp. 55-56: The gross structural differences in the C_4 path allow outer mesophyll cells to pump CO_2 into inner bundle sheath cells,[130] wherein ordinary C_3 fixation occurs. The raising of CO_2 concentration and lowering of O_2 concentration in the inner cells suppresses photorespiration. Offsetting the cost in energy of pumping (two extra ATP's per CO_2) is the prevention of PR, for a large net gain in fixation over C_3 plants. C_4 leaves also have higher conductance for entry of CO_2. C_4 as an adaptation to today's high atmospheric oxygen concentration is not perfect, however, as C_4 plants generally require somewhat high temperatures to photosynthesize rapidly.

C_3 plants undoubtedly have made their own, "lesser" adaptations to high oxygen levels. During episodes of fast photosynthesis where PR is likely to be a threat, their fixation enzyme (RuDP-CO_2ase) is "allosterically" altered by PS-dependent changes in pH and cation content of the chloroplast.[131,132] It then makes fewer "mistaken" acceptances of O_2. Present C_3 plants seem to require some residual PR. Soybeans suffer excess vegetative growth and poor reproduction in low-oxygen atmospheres,[133] as if overnourished with nitrogen. This result tempers the hope of abetting yields of legumes by lowering PR (page 55).

Long-lasting suppression of PR chemically seems possible in the laboratory,[102] but may be far less practical than the effort to breed crops with low PR, perhaps with the C_4 path itself. C_3 and C_4 plants are not genetically distant; both occur within single genera.[134] Natural species intermediate between C_3 and C_4 have been found,[135] and C_3 x C_4 hybrids have been made.[134] Stabilization of the whole set of C_4 traits very likely must be done trait-by- trait, perhaps using haploid lines of plants[136] for research or actual breeding.

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68. Electrolytic cells operate[75] with nearly 100% current-efficiency at $E \simeq 1.6$ volts, whereas theoretical miniumum voltage $E^0 = 1.23$ V. The minimum free energy used per mole of H_2 formed is $2E^0F$, or 0.77 of the actual usage $2EF$, where F = Faraday's constant.

69. Reference 75 as a whole reveals that end-uses which consume most energy are also most liable to improvement. Consider the automobile's efficiency, which might be doubled without radical technology.

70. In generating hydrogen from nuclear energy with intermediate conversion to electricity, the efficiency is (0.315) for nuclear → electrical energy times (0.77) for electrical → chemical energy, for a net of 24%.

In reforming methane to hydrogen, efficiency is perhaps 80%, such that energy consumed is 1.25 times the minimum from water to H_2, or (1.25) (356.3 kJ per $3/2$ mole H_2) = 445.4 kJ. Overall efficiency is 54%, such that energy consumed from H_2 to NH_3 (for compression, heating losses, etc.) is

$$\underbrace{\frac{339.9\text{ kJ}}{0.54}}_{\substack{\text{total of actual energy}\\ \text{consumed per mole of NH}_3}} - \underbrace{445.4\text{ kJ}}_{\substack{\text{energy to}\\ \text{form } 3/2\ \text{H}_2}} = 184.1\text{ kJ} .$$

Nuclear-derived H_2 should cost (356.3 kJ per mole of NH_3)/0.24 efficiency = 1484.6 kJ. Added to 184.1 kJ in the strict Haber process $3/2\ H_2 + 1/2\ N_2 \rightarrow NH_3$, this yields an energy of 1668.7 kJ per mole of NH_3. This in turn implies a total efficiency of 339.9 kJ/1668.7 kJ = 20% . It is presumed here that the strict Haber process uses energy in the new nuclear scheme at the same efficiency as in the old way. (Perhaps nuclear heat is used directly, or else fossil fuels continue to be used to heat the N_2/H_2 mixtures.)

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amounts to 12 times the food energy. The expenditure on-farm is so high because the U.S. diet includes much fresh produce which ranges up to 50:1 in ratio of "cultural" to food energies. Even the least-subsidized crops, the grains, use much cultural energy. Corn[14] at 6670 kg/ha (100 bu/acre) consumes 26.9 x 10^6 kJ/ha in subsidies and yields 31.0 kJ/ha of food value for direct human consumption.

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76. M. G. Bowman, "Chemistry of Thermochemical Cycles from U.S.A. Programs," presented at A.I.M. Intern. Conf. on Hydrogen and its Prospects (Association des Ingénieurs Electriciens Sortis de L'Institut Électrotechnique Montefiore Liege), Liege, Belgium, 15-18 November, 1976.

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